

Biodegradation of Pro-oxidant Filled Polypropylene Films and Evaluation of the Ecotoxicological Impact

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Published online: 10 April 2017
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Abstract The biodegradability of calcium stearate (CaSt) and cobalt stearate (CoSt) filled polypropylene (PP) films were investigated in this work. The PP films were prepared using melt blending technique followed by hot press moulding. On the basis of their tensile properties, the optimum amount of pro-oxidants was taken as 0.2 phr. Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used for the characterization of optimized films. Presence of pro-oxidant in the PP was confirmed by the FTIR studies. Addition of pro-oxidants in the films decreased the thermal stability as revealed by TGA analysis. Crystallinity of the pro-oxidant filled PP decreased with addition of pro-oxidants as shown by DSC. The maximum biodegradation of CaSt and CoSt containing PP films was shown 7.65 and 8.34%, respectively with 0.2 phr. Both the microbial test and plant growth test (on corn and tomato) indicated that biodegradation intermediates were non toxic.

Keywords Polypropylene · Pro-oxidant · Physico-mechanical · Biodegradability · Ecotoxicological impact

Introduction

Polypropylenes (PP) are extensively used as a flexible packaging material e.g. trash bags due to its low cost, good mechanical strength, hydrophobic nature, chemical resistance, effective water and gas barrier properties and ease of processability [1]. PP are petroleum derived products mainly combination of carbon and hydrogen. High molecular weight and hydrophobic nature make it water resistance, inhibit to microbial attack, increase self life and highly resistance to degradation. Therefore, accumulation of PP in different land sites leading to long term economical, environmental and waste management problem. Recycling of PP is one of the best solutions for this but it produces inferior quality products. The environmental problem should be reduced by producing harmless material and by proper management of PP waste materials. So, the searching and studying of new composition of materials, that can enhance the degradation of PP by various means has become very demanding to manage such environmental problems [2, 3].

Pro-oxidants are basically transition metal ion complexes. They are added in the PP in the form of either steirates or other organic ligand complexes including thermal or photo oxidation. Iron stearate (Fe^{3+}), magnesium stearate (Mn^{2+}) and cobalt stearate (Co^{2+}) [4, 5] are the most used pro-oxidants in the polyolefins. Among them, Fe^{3+} initiates photo oxidative degradation. Mn^{2+} and Co^{2+} initiate thermo oxidative degradation process and decreasing the molecular mass of PP to a level where microorganisms attack is possible. Pro-oxidant containing PP has demonstrated that the use of suitable pro-oxidant on the conventional low density

Electronic supplementary material The online version of this article (doi:10.1007/s10924-017-1016-3) contains supplementary material, which is available to authorized users.

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polyethylene (LDPE) film increases substantial oxidation of the films. Pro-oxidants filled materials degraded through free radical chain reaction taking oxygen from the atmosphere. The primary products of degradation are hydroperoxides, which can thermolyse or photolyse under the catalytic action leading to chain scission and production of low molecular weight oxidation products such as carboxylic acid, alcohols, ketones and low molecular weight hydrocarbons [6]. Pro-oxidants also modify the hydrophilic nature of polymeric material surface, which is responsible for microbial attack [7].

We would expect that PP will degrade and biodegrade but it has inverse relationship between molecular weight and biodegradability. A number of studies have been reported on the degradation behaviour of PP through various means [8–12]. In the last two decades, more investigations concerning the degradability of PP through blending of degradable natural polymer such as cellulose [3], starch [13–16] and poly(lactic acid) [17, 18] etc and isolated microorganisms, have been reported. Madhu et al. [19] studied the degradability of high density polyethylene/poly(lactic acid) with/without compatibilizer and pro-oxidant (cobalt stearate). They observed that the percentage crystallinity of PLA decreased after pro-oxidant addition due to the reorganization of the polymer chains in the blends caused by CoSt. Addition of cobalt stearate increases the degradation of HDPE and HDPE/PLA blends. Santhoskumar et al. [20] studied the biodegradability after the photodegradation of cobalt (Co) 12-hydroxyl oleate filled PP in the presence of microbes. The authors reported that the rate of photodegradation of PP was very high with 3% Co 12-hydroxyl oleate. The biodegradation of Co 12-hydroxyl oleate filled photodegraded PP films up to 24% has been reported at the end of 45 days. Abrusci et al. [21] evaluated the degradation by carbon dioxide measurements using an indirect impedance technique. They observed that at 45 °C, degradation was more efficient and in particular in the more photo-degraded films containing Ca and Fe stearate where degradation extents reached values of 11.5% with *B. borstelensis* and 7–10% with the mixture of *Bacillus* (Mix). Montagna et al. [22] studied degradation of organic pro-degradant filled PP under two different environmental conditions (abiotic and biotic), and found that the use of 1,2-oxo-hydroxy additive effectively enhanced the degradation of PP under the natural weathering and soil conditions. Roy et al. [23] investigated the role of metal oxidation state of pro-oxidant on the degradation behavior of LDPE. They found that the oxidation state of the metal did not affect its ability to initiate and accelerate degradation. The results have shown that iron is primarily an effective photo-oxidant, while cobalt and manganese can act both as photo-oxidant as well as thermo-oxidant. But no appreciable research has been carried out on the

preparation of pro-oxidant filled PP films, specifically for their biodegradability.

After biodegradation, evaluations of environmental impact of biodegradation intermediates are important. It is very necessary to know the harmful effect of biodegradation intermediates of modified PP films. Microbial test and plant growth test are ecotoxicological tests generally used for the evaluation of toxicity of biodegradation intermediates [24, 25]. In the plant growth test, two plants are used to analyse the ecotoxicological impact of biodegradation intermediates of modified PP films. This is one of the available standard methods for the evaluation of toxicity of biodegradable intermediates [26, 27].

In this research work, an attempt has been made to develop biodegradable packaging films from pro-oxidant filled PP and evaluate the effect of pro-oxidant concentration on physical, chemical, thermal and morphological properties. Biodegradability of optimized pro-oxidant filled PP films was measured. The ecotoxicological impact of the biodegradation intermediates was evaluated by microbial and plant growth test.

Experimental

Materials

Polypropylene homopolymer pellets (Grade F110) were supplied by Haldia Petrochemicals Limited, India with MFI=11 g/10 min, melting temperature=165 °C and density 0.9 g cm⁻³ [28]. Calcium stearate (6.6–7.4% Ca basis) with molecular weight=607.02 was provided by Sigma–Aldrich as received. Cobalt stearate (Co, 9–10%) with molecular weight=625.89 was purchased in pellet form from Alfa Aesar, Johnson Matthey Chemical India Private Limited. Nutrient agar and hydrochloric acid having 35% concentrations was purchased from Hi-Media Laboratories Pvt. Ltd., India. Corn seeds and tomato plants were purchased from Arman Seed Farm, Patiala, ethanol was purchased from Changshu Yangyuan chemical, China.

For the biodegradation test, Delhi Jal Board (compost plant) at Okhla, New Delhi, India provided the digested municipal solid waste (matured compost). The compost properties were evaluated as per the American Public Health Association [29]. Oversized materials such as glass, metal, stone etc. were separated out by screening through 1 mm mesh sieve. The total organic carbon present was 34% and total Kjeldahl nitrogen was 2.2% in the compost sample. The water holding capacity of compost was 60–65%, measured after oven drying at 105 °C for overnight. The C:N ratio of the compost was 15.3. Total dry solids of 81% and volatile solids of 18% were present in the

compost. The pH of the compost was 7.2, measured as per procedure of reference [30].

Pro-oxidant Filled Polypropylene Blend Preparation

Pro-oxidant filled PP blends based on calcium and cobalt stearate, in varying ratio(s), were prepared in an internal mixer (Haake Poly Lab, Germany). The rotor speed was kept 60 rpm at 190 °C for 4 min with a fill factor of 0.8. The ingredient were mixed manually before being loaded into the mixer. The extrudate was passed through a two-roll mill with a nip gap of 2 mm, maintaining the rolls at room temperature. The compositions of the prepared pro-oxidant filled PP are described in Table 1.

Film Preparation

The PP and pro-oxidant filled PP films were casted at 185 °C and 400 kN m⁻² pressures in hot press moulding for 2 min to obtain 80–85 μm thick films. Sticking of molten material to mold plates was prevented by putting Teflon sheets in between them.

Characterization

Tensile Test

The Universal Testing Machine (Z010, Zwick-Roell, Germany) was used to measure the tensile strength at yield and elongation at break (E_b) for the films. The test was

Table 1 Compositions of polypropylene and pro-oxidant filled polypropylene

Sr. no.	Polymer	Composition		
		PP (phr)	CoSt (phr)	CaSt (phr)
1	PP	100	0	0
2	PP100CoSt0.2	100	0.2	0
3	PP100CoSt0.4	100	0.4	0
4	PP100CoSt0.6	100	0.6	0
5	PP100CoSt0.8	100	0.8	0
6	PP100CoSt1.0	100	1.0	0
7	PP100CoSt1.5	100	1.5	0
8	PP100CoSt2.0	100	2.0	0
9	PP100CaSt0.2	100	0	0.2
10	PP100CaSt0.4	100	0	0.4
11	PP100CaSt0.6	100	0	0.6
12	PP100CaSt0.8	100	0	0.8
13	PP100CaSt1.0	100	0	1.0
14	PP100CaSt1.5	100	0	1.5
15	PP100CaSt2.0	100	0	2.0

conducted according to ASTM D 882-91 standard. The rectangular shaped specimens for tensile test were prepared by strip-sample cutter. The clamp separation kept 125 mm with cross head speed 12.5 mm min⁻¹.

Fourier Transform Infrared Spectroscopy

The change in PP film structure due to the addition of pro-oxidant was analysed by Perkin Elmer fourier transform infrared spectroscopy (FTIR) spectrophotometer. The scanning range was set from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. The spectrum software (spectrum 100) was used to analyse the obtained spectra.

Thermogravimetric Analysis

TG and DTG of the pro-oxidant filled PP films were analysed on a TA Instruments Q-500 thermogravimetric analysis (TGA) analyzer. The analyses were done under the pure nitrogen condition with flow rate 50 ml min⁻¹. The weight of the samples was taken 5–10 mg and heating rate was kept 20 °C min⁻¹ from ambient temperature to 750 °C.

Differential Scanning Calorimetry Analysis

Thermal properties of pro-oxidant filled PP films was measured under the nitrogen atmosphere using differential scanning calorimeter (DSC) Model 200F3, Netzsch, Germany. The films were heated from room temperature to 200 °C at heating rate of 10 K min⁻¹. The weight of films was 5–10 mg. The degree of crystallinity of pro-oxidant filled PP films was estimated [by using 163 J g⁻¹ as heat of fusion (ΔH^0) for 100% crystalline PP] according to Eq. 1 [31]:

$$\text{Crystallinity (\%)} = \frac{\Delta H}{\Delta H^0} \times 100 \quad (1)$$

where, ΔH^0 is the heat of fusion of 100% crystalline PP and ΔH is the heat of fusion of modified PP films.

X-Ray Diffraction

XRD was used to assess the effect of pro-oxidant on the crystallographic structure of modified PP films with an X-ray diffractometer Philips Xpert (Almelo, Netherlands). The instrument was operated at 40 kV and 20 mA with a Cu-K α radiation wavelength (λ) of 1.54 Å. The speed of scanning during the test was 5° min⁻¹ and diffraction angle was 5°–35°.

Scanning Electron Microscopy

SEM analyses were carried out using a JEOL scanning electron microscope (JSM 6510-LV, Tokyo, Japan) to assess the fracture surface morphology. All films were metalized with 15 nm gold film to avoid charging under an electron beam in a high vacuum automatic sputter coater model JFC-1600, Japan.

Biodegradability

Biodegradation of PP and pro-oxidant filled PP films was evaluated by measuring carbon dioxide (CO₂) produced during incubation at 58 °C for 45 days according to the ASTM standard D 5338-11 [32]. The tests were performed in three replicates and results were averaged. The standard deviation of biodegradation was ±2. The mass of CO₂ produced from composting was determined using indirect method (acid-base titration). In the blank treatment, only compost material was used. Whereas in the positive treatment, we have added micro crystalline cellulose powder sample with the compost material and neat PP film was added in compost material as negative treatment. The percent biodegradation was calculated as the ratio of average CO₂ production from films and the theoretical (CO₂)_{th} using following equation.

$$(\%) \text{ Biodegradation} = \frac{(\text{CO}_2)_{\text{test}} - (\text{CO}_2)_{\text{blank}}}{(\text{CO}_2)_{\text{th}}} \times 100 \quad (2)$$

where, (CO₂)_{th} is the theoretical mass of CO₂ in gram evolved from the test sample. (CO₂)_{test} is the cumulative mass of evolved CO₂ in gram from test reactor and (CO₂)_{blank} is the cumulative mass of evolved CO₂ in gram from the blank reactor.

Evaluation of Ecotoxicological Impact of Degradation Intermediates From Grafted Film

To analyse the effect of biodegradation intermediates on the quality of compost product, we performed the microbial toxicity test and plant growth toxicity test.

Microbial Toxicity Test

For toxicity evaluation of PP and grafted PP substrate after biodegradation, samples of compost after biodegradation test were taken. 1 g of each compost sample was immersed in 10 ml of autoclaved distilled water, vortexed for 1 min and then kept undisturbed for 30 min. The compost suspension was serial diluted to a factor of 10⁻³ and then 100 μl of each of 10⁻¹, 10⁻² and 10⁻³ dilution [33] factor was inoculated on nutrient agar plate plate for the estimation of

the number of bacterial colony-forming units (CFUs) per ml [24, 34]. Plates were incubated at 37 °C in an incubator (Model NSW-152 of Narang Scientific Works Pvt. Ltd., India) for 24 h. The microbial population of compost was estimated as the number of bacterial CFUs per ml of suspension as follows:

$$\text{CFU/ml} = \text{number of colonies per ml plated} / \text{Total dilution factor} \quad (3)$$

With the same weight of compost was used as control.

Plant Growth Test

The medium used for the plant growth tests was 2:1:1 mixture of soil, perlite and compost (after biodegradation test). The plant growth test was performed with tomato (*Solanum lycopersicon*) and corn (*Zea mays*) according to the guideline of organization for economic co-operation and development (OECD 208) Terrestrial Plant Growth Test [26]. Tomato plants and corn seeds (30 and 90) were sown in the medium described. Three replicates were done for the each test material and control. The plants were grown under the controlled condition, (22 ± 10 °C, humidity 70 ± 25% and 16 h light/8 h dark) for 3 weeks. The emerged seedlings were counted after 21 days and the dry weight of the plants above the soil was determined at 75 °C until constant weight was achieved.

Results and Discussion

Tensile Test

The tensile properties such as tensile strength, tensile modulus and elongation of the PP and pro-oxidants containing PP films are shown in Table S1. The neat PP had tensile strength of 38.3 MPa and elongation 3.6%, which decreased on the addition of pro-oxidants due to the melt blending at 180 °C, pro-oxidant might have oxidized the PP to some extent resulting in low tensile strength. With increase in the amount of pro-oxidant, tensile strength, PP100CaSt2.0 and PP100CoSt2.0 had the lowest tensile strength amongst all of films. With addition of 0.2 phr calcium stearate and cobalt stearate the tensile strength reduce to 34.6 and 34.7 MPa. But, on further increasing the proportion of calcium stearate and cobalt stearate, i.e., up to 0.4 phr, the tensile strength drastically decreased to 24.1 and 24.9 MPa. The blend optimized with pro-oxidant concentration (0.2 phr) to get the strength properties in the desired range (above 30 MPa). The films of PP100CaSt0.2 and PP100CoSt0.2 showed lower value of E_b and all other composition are also shown lower value of E_b in comparison with PP. This trend of tensile strength and elongation

at break is shown in Fig. S1 and S2. The tensile modulus of the all composition lower than PP but PP100CaSt0.2 and PP100CoSt0.2 showed near to PP. Therefore, PP100CaSt0.2 and PP100CoSt0.2 was chosen as optimum. Further studies such as FTIR, DSC, TGA, SEM, XRD and biodegradability were done on these two optimized pro-oxidant filled PP films.

Fourier Transform Infrared Spectroscopy

The FTIR peaks of PP, PP100CaSt0.2 and PP100CoSt0.2 are shown in Fig. 1. The intensity of peak at 1560 cm^{-1} indicates the presence of metal stearate, which can be attributed to asymmetric vibration stretching of the carbonyl group coordinated to the metal ion [23]. This confirms the presence of pro-oxidant in the PP blended samples.

Thermogravimetric Analysis

The weight loss behaviour of PP, PP100CaSt0.2 and PP100CoSt0.2 films were studied in nitrogen atmosphere. The TG and DTG curves of PP, PP100CaSt0.2 and PP100CoSt0.2 films are shown in Fig. 2. T_i is the initiation degradation temperature of the films at 5% loss of weight and final temperature (T_f) corresponds to 95% loss of weight; T_i and T_f are summarized in Table 2. The T_i of the pro-oxidant filled PP films was lower than the neat PP film. It indicates that the degradation of PP films increased on addition of pro-oxidant. This is mainly because of initiation of degradation due to presence of metal ions in the pro-oxidant filled PP films [20]. T_f of the pro-oxidant filled PP films was also lower than the PP film. The PP,

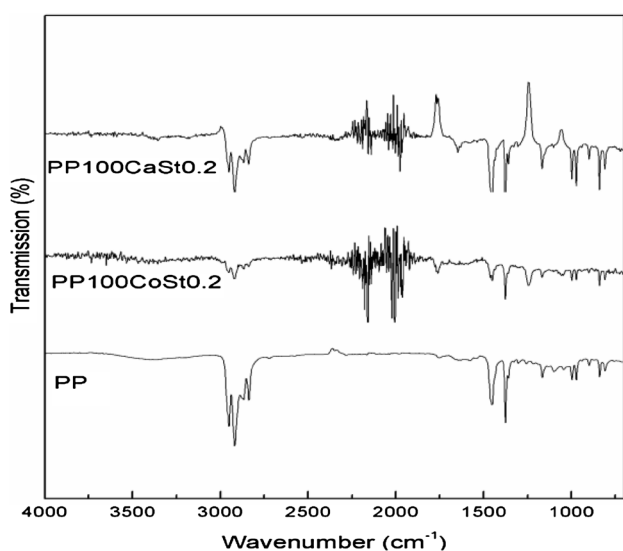


Fig. 1 FTIR results of PP and pro-oxidant filled PP

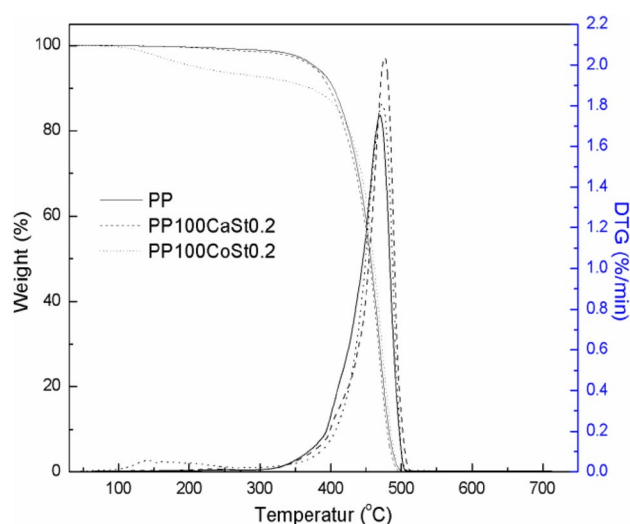


Fig. 2 TGA curves of PP and pro-oxidant filled PP films

PP100CaSt0.2 and PP100CoSt0.2 films showed thermal stability up to 379.21 , 375.85 and 211.34 °C as shown in Fig. 4.

Differential Scanning Calorimetry Analysis

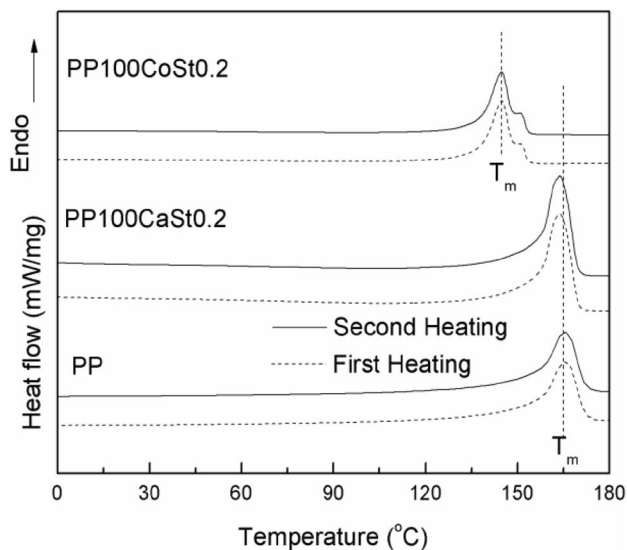
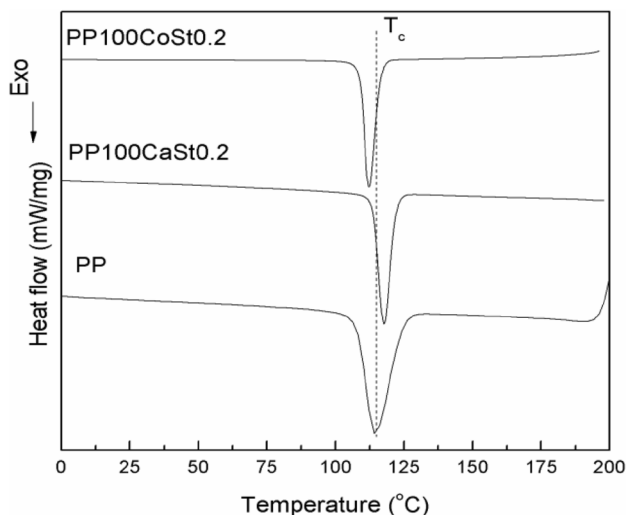
PP is a semicrystalline thermoplastic polymer which, on application of heat, undergoes a process of fusion or melting wherein the crystalline character of the polymer is destroyed. The heating and cooling curves of PP and pro-oxidant filled PP films are shown in Figs. 3 and 4. The curves in Figs. 3 and 4 show the second heating obtained from DSC of PP, PP100CaSt0.2 and PP100CoSt0.2 films. The melting temperature (T_m), crystallization temperature (T_c), enthalpy of fusion (H_f) and crystallinity of the films are listed in Table 3. The crystallinity of the films is calculated from heat of fusion by using Eq. 1. The T_m of pro-oxidant filled PP films is lower than that of the neat PP. This indicates that the susceptibility to thermal degradation increases with addition of pro-oxidant [35]. The crystallinity of pro-oxidant filled PP is also lower than that of PP due to the insertion of the side and/or functional groups [22]. Pro-oxidants reduces the crystallinity, and makes pro-oxidant filled PP more susceptible to attack of microorganisms [35].

X-Ray Diffraction Measurement

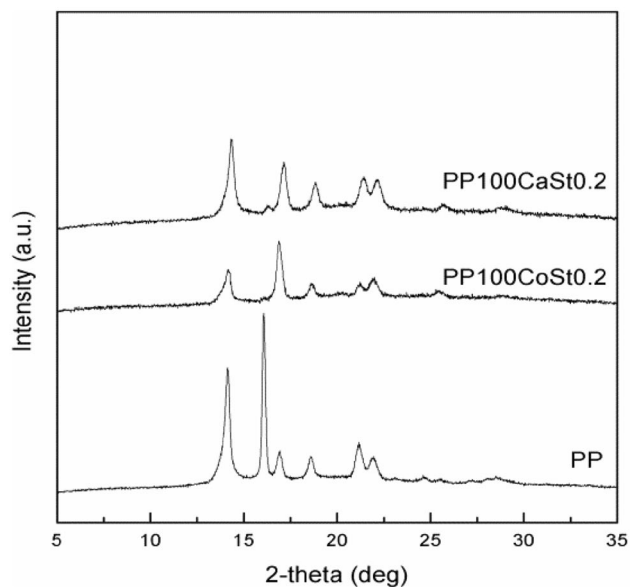
The XRD patterns of the samples are shown in Fig. 5. The diffraction peaks of PP show at $2\theta = 14.1^\circ$, 16.9° , 18.6° , 21.1° and 21.9° which correspond to the α -monoclinic form of PP [18]. The addition of calcium and cobalt stearate did not lead to any changes in the diffraction peaks of blended PP [19], though there is a decrease in the intensity.

Table 2 TGA data of PP and pro-oxidant filled PP films

Polymer films	T_i (°C)	T_f (°C)	Weight loss (%)
PP	379.21	487.22	100
PP100CaSt0.2	375.85	484.86	100
PP100CoSt0.2	211.34	488.84	100

**Fig. 3** DSC thermograms of PP and pro-oxidant filled PP films**Fig. 4** DSC thermographs of PP and pro-oxidant filled PP films**Table 3** DSC data of PP and pro-oxidant filled PP films

Polymer films	T_m (°C)	T_c (°C)	ΔH (J g ⁻¹)	Crystallinity (%)
PP	165.5	114.5	103.7	63.61
PP100CaSt0.2	163.56	122.3	77.31	47.42
PP100CoSt0.2	144.47	114.5	78.41	48.10

**Fig. 5** XRD results of PP and pro-oxidant filled PP films

Which clearly indicates that the addition of calcium and cobalt stearate decreases the crystallinity of the PP films.

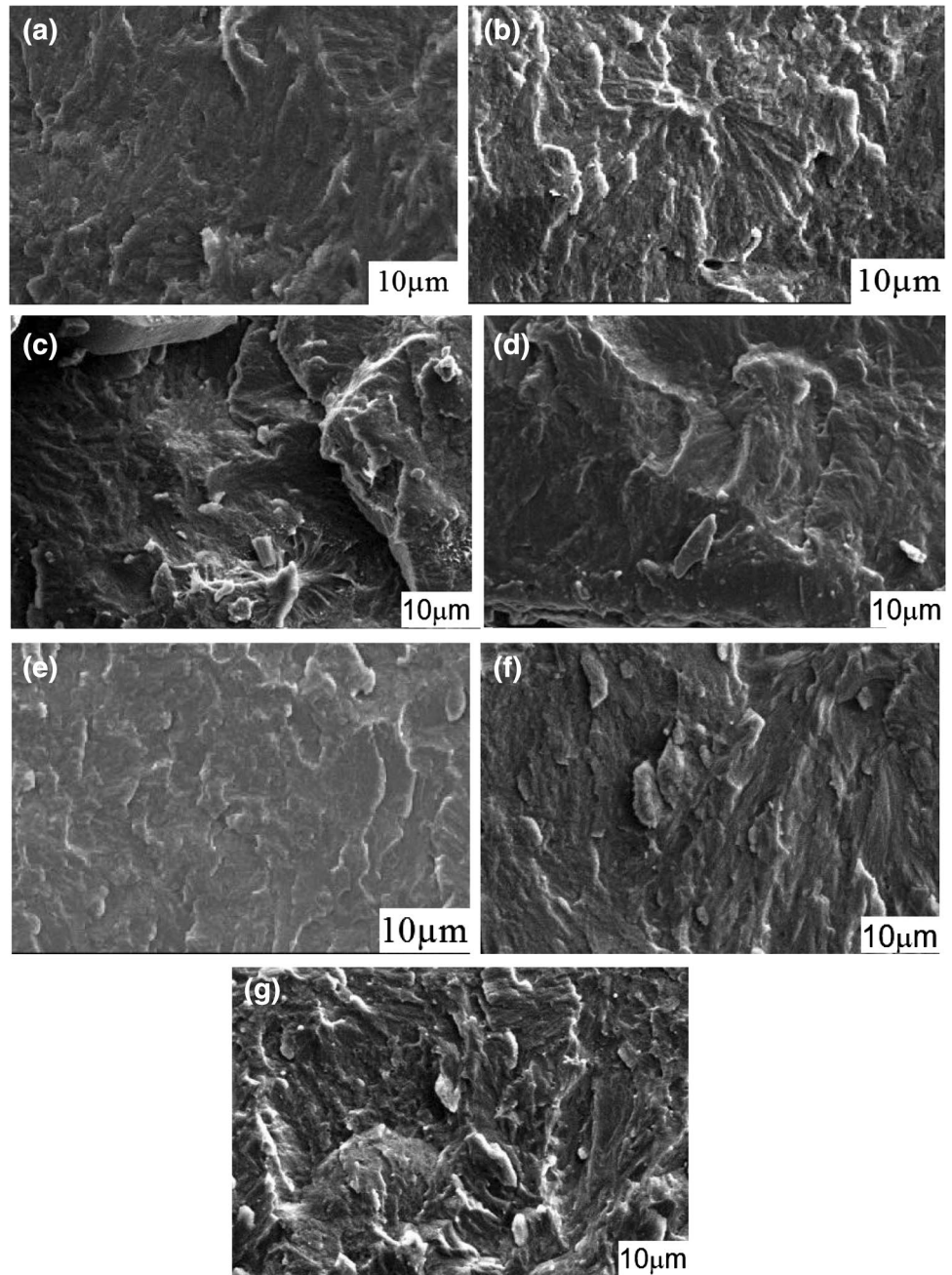
Scanning Electron Microscopy

Figure 6 shows the scanning electron micrographs of PP, PP100CaSt0.2, PP100CaSt0.8, PP100CaSt2.0, PP100CoSt0.2, PP100CoSt0.8 and PP100CoSt2.0 films. These SEM micrographs were taken on cryofractured surface (in longitudinal direction) of the films. Addition of calcium stearate and cobalt stearate did not significantly change the morphology of the PP, in PP100CaSt0.2 and PP100CoSt0.2 films. Tensile strength of PP100CaSt0.2 and PP100CoSt0.2 is quite similar to PP due to insignificant change in morphology. But, different morphology (uneven surface) is seen in the film samples of PP100CaSt0.8, PP100CaSt2.0, PP100CoSt0.8 and PP100CoSt2.0.

Biodegradability

In general, tensile strength of the polymer decreases on blending with any low molecular weight material pro-oxidant. In addition, during the melt blending, strength decreases due to some action of pro-oxidant on PP. Therefore, the concentration of pro-oxidant was optimized by conducting the experiments with (0–2 phr) concentration of the pro-oxidant to retain the tensile strength in the desired range (>30 MPa). The optimum concentration of pro-oxidant was found to be 0.2 phr for both the pro-oxidants (results not shown).

Fig. 6 SEM images of **a** PP, **b** PP100CoSt0.2 **c** PP100CoSt0.8, **d** PP100CoSt2.0, **e** PP100CaSt0.2, **f** PP100CaSt0.8 and **g** PP100CaSt2.0



The biodegradability of PP, PP100CaSt0.2 and PP100CoSt0.2 was determined according to the guideline of ASTM standard D 5388-11. In this work, biodegradation of pro-oxidant filled PP in terms of CO_2 evolution was performed. Cellulose was used as positive control reference material and neat PP film was taken as negative reference. The microorganisms present in the compost should mineralize the biodegradable substrate of the pro-oxidant filled PP films into carbon dioxide and water molecules. Biodegradation of pro-oxidant filled

PP was evaluated by estimating the amount of evolved CO_2 from the samples. Biodegradability of all the samples in 45 days is shown in Fig. 7. The biodegradability sequence in terms of percentage biodegradation was: cellulose (76%) > PP100CoSt0.2 (8.34%) > PP100CaSt0.2 (7.65%) obtained by using Eq. 2 in 45 days. The results showed that pro-oxidant filled PP PP100CoSt0.2 and PP100CaSt0.2 are highly biodegradable than neat PP due to the cleavage of weak linkage and chain scission [36]. PP film showed non-biodegradability obviously

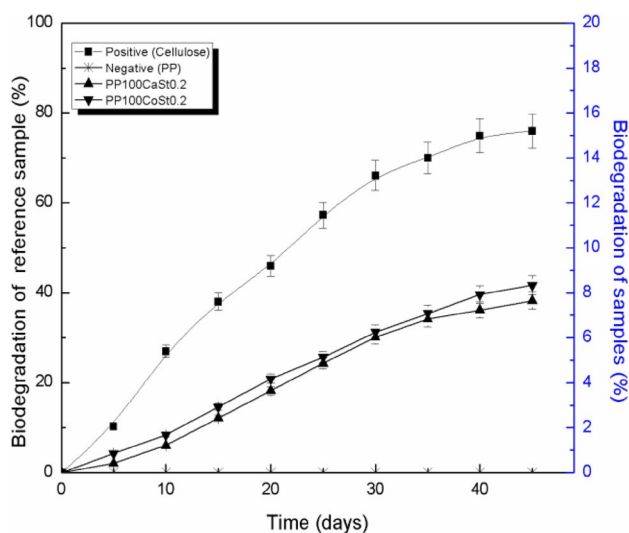


Fig. 7 Biodegradability of PP and pro-oxidant filled PP films

due to its hydrophobic property and high molecular weight, which inhibited the microorganism activity. Incorporation of cobalt stearate and calcium stearate into PP increased the functional groups and decreased the crystalline structure in pro-oxidant filled PP films [22]. It also increased the thermal degradation of the pro-oxidant filled PP films. Thermal degradation helps in chain scission and reduce pro-oxidant filled PP films into low molecular weight products like hydroperoxides and carbonyl species (ketones/esters). These low molecular weight products are easily consumed by the microorganisms [21]. The low crystallinity of the pro-oxidant filled PP films also makes them susceptible to microorganisms attack [35]. After the consumption of these low molecular weight compounds as a energy source, they release CO_2 , H_2O and biomass [37]. Cobalt stearate filled PP

Table 4 The number of bacterial colonies (CFUs) from water extract of compost containing different samples

Polymer sample	CFU/ml count $\times 10^4$
Control	0.2
Cellulose	Bacterial lawn (uncountable)
PP	0.3
PP100CaSt0.2	0.4
PP100CoSt0.2	0.7

film shows higher biodegradability than the calcium stearate filled PP due to the higher susceptibility towards the thermal degradation and more availability of low molecular weight products for the microbial attack.

Toxicity Evaluation by Microbial Toxicity Test

The number of colony forming bacteria in the soil extracts is shown in the Table 4. It can be seen that the blank sample was having CFU count of 0.2×10^4 and the cellulose gave highest number (uncountable) of CFU. CFU count in the all compost samples of grafted films are close to or higher than blank sample indicating the normal growth of the bacteria in the soil sample of grafted films. Therefore, it can be concluded that the degradation products from these grafted samples are non-toxic in nature.

Toxicity Evaluation by Plant Growth Test

To confirm the suitability of composted PP films as growth medium for the plant growth test, pH of the medium was measured. The optimal pH range for the growth of most plants is about 5.5 [38]. The solubility and availability of nutrients in the growth medium are affected by extremely low or high pH. In this study, the pH of the medium was adjusted to 5.8–6.0, which is near to optimum value for the plant growth.

To know the eco-toxicological effect of biodegradation products of grafted PP on the quality of the medium, plant growth test have been carried out with tomato and corn [26]. After 21 days test, the visual evaluation of seedlings (corn and tomato) in the growing medium indicated that average amount of plant emergence is 100%. There was no quality difference in case of both the plants between control and test samples (Figs. 8, 9). Additionally, after 21 days of growth, plants have been harvested, dried and gravimetric measurements have been made. Growth of corn and tomato measured as percentage of dry weight against the control is almost 100% as shown in Fig. 10.

Conclusions

Pro-oxidant (calcium stearate and cobalt stearate) filled PP films have been successfully moulded in hot moulding press after mixing in an internal mixer. The ratio of PP/

Fig. 8 Growth of tomato in compost (after 45 days biodegradation) of **a** control, **b** cellulose, **c** PP, **d** PP100CaSt0.2 and **e** PP100CoSt0.2

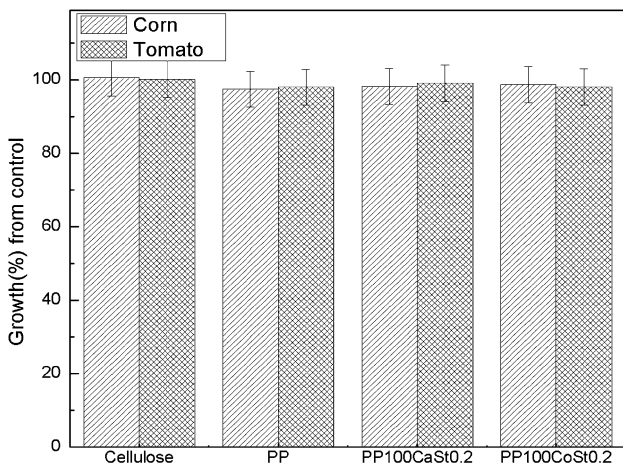
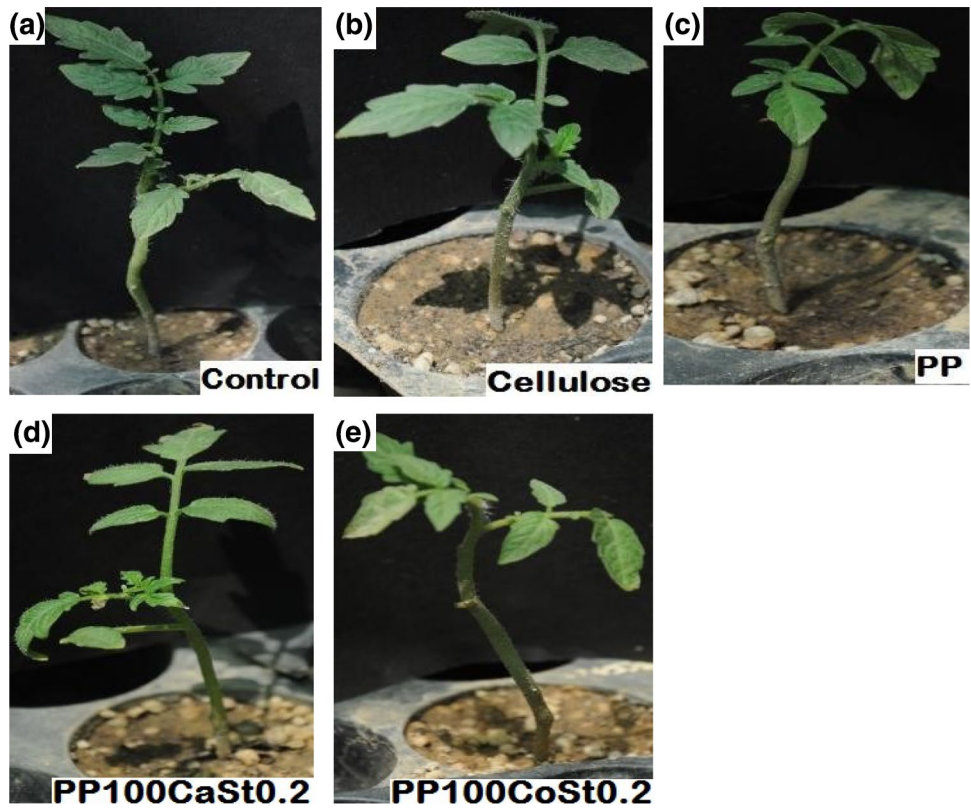
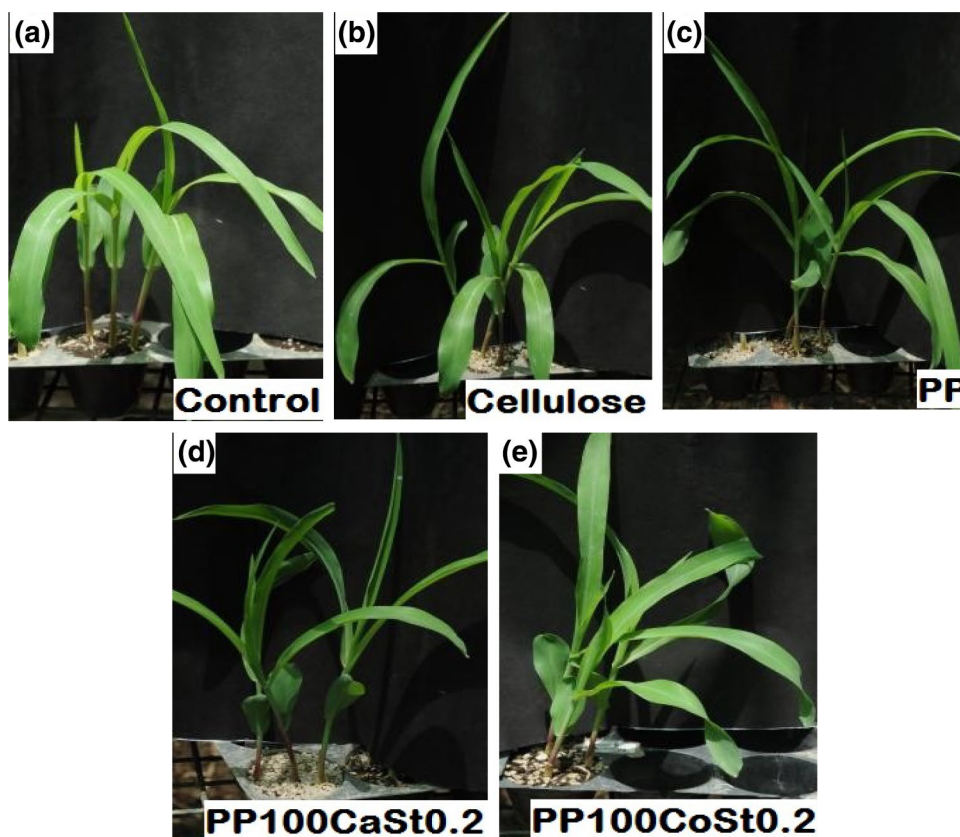


Fig. 9 Growth of corn and tomato measured as percent of dry weight against the control (*Error bars* represent the standard deviation of three replicates)

pro-oxidant was optimized on the basis of their mechanical properties. PP100CaSt0.2 and PP100CoSt0.2 are found to be optimum composition, therefore, their physical, chemical and biodegradable properties have been evaluated. FTIR peak at 1560 cm^{-1} showed the presence of metal stearate in the compositions. TGA analysis showed that the thermal degradation of PP films increases with addition of cobalt stearate and calcium stearate. The crystallinity of cobalt stearate and calcium stearate filled PP films has decreased as confirmed by the DSC and XRD studies. The degree of biodegradation has increased with addition of cobalt stearate and calcium stearate in PP films. Biodegradability of the PP, PP100CoSt0.2 and PP100CaSt0.2 are 0, 8.34 and 7.65% respectively after 45 days incubation period. Biodegradation intermediates are non toxic in

Fig. 10 Growth of corn in compost (after 45 days biodegradation) of **a** control, **b** cellulose, **c** PP, **d** PP100CaSt0.2 and **e** PP100CoSt0.2



nature as confirmed by the microbial test and plant growth test (corn and tomato).

Acknowledgements The project was funded by Department of Atomic Energy—Board of Research in Nuclear Sciences (DAE-BRNS), Bhabha Atomic Research Centre, Govt. of India through Sanction No. 35/14/08/2014-BRNS. Special thanks to Dr. Debaprasad Mandal, Assistance Professor, Department of Chemistry, IIT Ropar, Punjab for performing DSC testing.

References

- Briassoulis D, Aristopoulou A, Bonora M, Verloot I (2004) *Bio-syst Eng* 88:131–143
- Hamilton JD, Sutcliffe R (1997) *Ecological assessment of polymers*. Van Nostrand Reinhold, New York
- Kaczmarek H, Oldak D, Malanowski P, Chaberska H (2005) *Polym Degrad Stab* 88:189–198
- Jakubowicz I (2003) *Polym Degrad Stab* 80:39–43
- Albertsson AC, Barenstedt C, Karlsson S (1993) *J Polym Environ* 1:241–245
- Khabbaz F (2001) *Environmentally Degradable Polyethylene: Effects of Additives and Environment on the Degradation and Degradation products*. Ph. D. Thesis, Department of Fiber and Polymer Technology, KTH School of Chemical Science and Engineering, Sweden
- Konduri MK, Koteswarareddy G, Rohini Kumar D, Venkata Reddy B, Lakshmi Narasu M (2011) *J Appl Polym Sci* 120:3536–3545
- Ballice L, Reimert R (2002) *Chem Eng Process* 41:289–296
- Bockhorn H, Hornung A, Hornung U (1999) *J Anal Appl Pyrolysis* 48:93–109
- Gao Z, Kaneko T, Amasaki I, Nakada M (2003) *Polym Degrad Stab* 80:269–274
- Chan J, Balke S (1997) *Polym Degrad Stab* 57:127–134
- Nakatani H, Suzuki S, Tanaka T, Terano M (2007) *Polym Int* 56:1147–1151
- Steller R, Meissner W (1998) *Polym Degrad Stab* 60:471–480
- Ramis X, Cadenato A, Salla J, Morancho J, Valles A, Contat L, Ribes A (2004) *Polym Degrad Stab* 86:483–491
- Morancho J, Ramis X, Fernández X, Cadenato A, Salla J, Vallés A, Contat L, Ribes A (2006) *Polym Degrad Stab* 91:44–51
- Orhan Y, Hrenovic J, Buyukgungor H (2004) *Acta Chim Slov* 51:579–588
- Jain K, Madhu G, Bhunia H, Bajpai PK, Reddy MS (2014) *J Polym Mater* 31:63–68
- Jain K, Madhu G, Bhunia H, Bajpai PK, Nando GB, Reddy MS (2015) *J Polym Eng* 35:407–415
- Madhu G, Bhunia H, Bajpai PK, Nando GB (2016) *Polym Sci Ser A* 58:57–75
- Santhoskumar A, Palanivelu K (2012) *Int J Polym Mater* 61:793–808
- Abrusci C, Pablos JL, Corrales T, Lopez-Marin J, Marin I, Catalina F (2011) *Int Biodeterior Biodegradation* 65:451–459
- Montagna LS, da Camargo Forte MM, Santana RMC (2013) *J Mater Sci Eng A* 3:123–131
- Roy P, Surekha P, Raman R, Rajagopal C (2009) *Polym Degrad Stab* 94:1033–1039
- Mallakpour S, Banihassan K, Sabzalian MR (2013) *J Polym Environ* 21:568–574
- Bardi MA, Munhoz MM, Auras RA, Machado LD (2014) *Ind Crops Prod* 60:326–334

26. OCED 208, Terrestrial plant growth test; OECD guidelines for Testing of Chemicals, 1984
27. Gong P, Wilke B-M, Strozzi E, Fleischmann S (2001) *Chemosphere* 44:491–500
28. Haldia Petrochemical Ltd., <http://www.haldiapetrochemicals.com/index.php?p=cms&id=11>. Technical Data Sheet (F-110 Pdf). Accessed 23 Feb 2017
29. Clesceri LS, Greenberg AE, Trussell RR (eds) (1989) Standard methods for the examination of water and wastewater, 17th edn. American Public Health Association (APHA), American Water Works Association (AWWA), Water Pollution Control Federation (WPCF), Washington, DC
30. Singh G, Kaur N, Bhunia H, Bajpai PK, Mandal UK (2012) *J Appl Polym Sci* 124:1993–1998
31. Anjum N, Gupta B, Riquet AM (2006) *J Appl Polym Sci* 101:772–778
32. ASTM, D. 5338: Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions 2011
33. Aneja K (2008) A textbook of basic and applied microbiology. New Age International, New Delhi, pp 235–236
34. Mallakpour S, Dehghani M, Sabzalian MR (2013) *J Polym Res* 20:85–91
35. Rosa D, Grillo D, Bardi M, Calil M, Guedes C, Ramires E, Frolini E (2009) *Polym Test* 28:836–842
36. Muthukumar T, Aravinthan A, Mukesh D (2010) *Polym Degrad Stab* 95:1988–1993
37. El-Arnaouty M, Abdel Ghaffar A, El Shafey H (2008) *J Appl Polym Sci* 107:744–754
38. Marschner H (1995) Functions of mineral nutrients: macronutrients. mineral nutrition of higher plants, 2nd edn. Academic Press, London, pp 299–312