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Biodegradation of Packaging Materials: Composting of Polyolefins

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Summary: The compostability of LDPE, PP and heterophasic E-P Copolymers was studied for 5 months under normal and accelerated composting environments. Bio-susceptibility of pre-UV (290 nm) treated films (~ 100μm, 5 X 5 cm) was measured by monitoring the weight loss, intrinsic viscosity [η], chain scission, functional group evolution (FT-IR) and surface morphology (SEM). It was found that with the increasing time of UV treatment, weight loss was increased in compost. Almost linear decrease in [η] was observed for irradiated and composted samples. The temperature of compost and extra addition of thermophilic microbes significantly influenced the biodegradation. In general, it was concluded that the composition of copolymer markedly affected the compostability and increased ethylene content, slowed down the microbial activity.

Keywords: biodegradation; composting; ethylene-propylene copolymers; photodegradation; polyolefins

Introduction

The long-term properties in the synthetic and natural polymers have attracted more interest during the last decades, as environmental concerns increased [1-2] due to the accumulation of municipal solid waste, generated by the commodity polymers. Although several formulations[3-4] filled with starch with pro-oxidants have been well documented in order to achieve the biodegradability in synthetic polymers, the development of inexpensive and real biodegradable materials with desirable mechanical properties is still under investigation. The recycled polymers loose their physical properties due to repeated thermal /oxidative degradation and this process itself uses oil-based energy, which make it more costly. Generation of energy[5] by the incineration of plastics is an economic and conventional route for waste management but the energy cost and waste transport including emission of toxic gases are key factors for environmental concerns. Now-a-days, there is increasing interest to recycle the polymers biologically, precisely by composting. [6] Composting is the transformation of organic material

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through decomposition into a soil-like material called compost. This process is beneficial over the traditional waste control methods from the point of view that it is environmental friendly and fairly safe way to convert the solid waste into biomass. The present work intends to investigate the compostability of additive-free homo and copolymers of polyolefins in normal and accelerated composting after short term UV exposure.

Experimental

Material

Commercial samples of isotactic polypropylene (PP, Koylene S 30330), low density polyethylene (LDPE, Indothene 16 MA 400) were obtained from M/s Indian Petrochemicals Corp. Ltd. Baroda, India and heterophasic ethylene propylene copolymers were obtained from M/s Himont Italia and after purification/fractionation,[7] the samples were designated as EPA & EPB of molar percentages of ethylene content, 40.9 and 6.1, respectively.

Preparation of Films and UV Irradiation

The photo-irradiation of the films was carried out in an accelerated weathering chamber (SEPAP 12/24) at 60 °C. The chamber consists of (4 x 400W) medium pressure mercury vapor lamps supplying radiation longer than 290 nm.

Viscosity Measurement

The intrinsic viscosity [η] dl/g, was measured by using successive dilution of only one solution (concen., 0.2 wt.%) at 135 ± 5°C in decaline.

The average number of scission(s) per single chain length[7, 8] is evaluated using the equation

$$p_{v,t} / p_{v,0} = (2/s^2)(e^{-1} + s - 1) \qquad (1)$$

where $p_{v,0}$ and $p_{v,t}$ represent the viscosity average chain length initially and at time *t* during the degradation process. Equation (1) is valid only for those cases where $p_{v,0}$ is small and for larger values of $p_{v,0}$:

$$s/p_{v,0} - 1 \approx s/p_{v,0} = \alpha \qquad (2)$$

where α is the degree of oxidative degradation. The α can be estimated by assuming that rate of breaking of links is proportional to the number of links, present at any time *t*. Thus :

$$-d(p_{v,t} - 1)/dt = k(p_{v,t} - s) \qquad (3)$$

where s links undergo scission out of a total $p_{v,t} = p_{v,0} - 1$ links, then upon integrating, the degree of degradation becomes:

$$\alpha = 1 - e^{kt} \qquad (4)$$

Moreover, the values of the specific rate constant k are usually small and it is possible to use the approximation : $\alpha = kt$ (5)

The average values of k were evaluated from the initial slope of the curve of α versus irradiation time using the relationship of Equation (4).

FT-IR Spectroscopy & SEM

FT-IR (Fourier Transform infrared 16 PC Spectrometer) was used to characterize the photo-products in the polymer films. The UV exposed films were placed in stoppered bottles containing osmium tetraoxide (2 % aqueous) and allowed standing for 48 h. The stained samples were dried under vacuum for 24 h at 50°C. The gold-coated samples were examined under electron microscope (Leica Cambridge Stereoscan 440 model) for morphological changes.

Incubation in Compost

The biodegradability tests of films (5 X 5 cm) were performed in a laboratory scale composter. The constitution[9,14] of compost used for biodegradability testing of photooxidised samples was > 30 % saw dust and 38 % cow dung with bread, shredded leaves and other vegetable waste. The moisture content was maintained to 50 ± 5 %.Total carbon percent was obtained by measuring the ash and it was 9.16 %. The carbon/nitrogen (C / N) ratio was evaluated from the average of 10 samples and was found 27 / 1. This composting pile was normal compost and temperature did not increase more than 42°C as enough water was sprayed periodically. The composting bin was heated from outside and maintained at 65 ± 5°C. Fertilizers were added from outside and C/N ratio was 35/1. Moisture content was < 45 ± 5 % and at this stage we added thermophilic microbes into the bin. The saw-dust, vegetable waste and cow dung ratio was 1 : 3 : 1 with carbon % of 9.13. The temperature profile of the compost during testing is shown in Figure 1, where composting temperature was varying with the temperature of the surrounding atmosphere.The biodegradability was determined by measuring the percent weight loss.

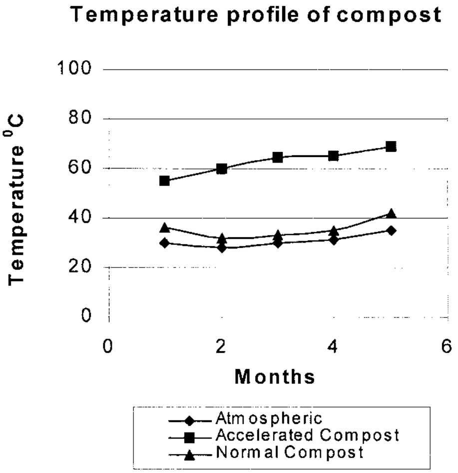

Figure 1. Temperature variation of compost during study

Result and Discussion

The weight loss of 0, 30 and 90 h irradiated, composted, polymer samples was measured periodically for 5 months, after careful washing with distilled water and drying in vacuum oven till constant weight. The mechanisms, changes in functional groups and surface morphology upon UV exposure of polyolefins and their copolymers have been well studied[10] where hydroxyl (3700-3200 cm^{-1}), hydrogen bonded hydroperoxide (3420 cm^{-1}), associated alcohols (3380 cm^{-1}), carbonyl / ketonic (1850-1550 cm^{-1}) and absorptions at 1712, 1722, 1740 and 1785 cm^{-1} have been assigned to carboxylic acid, ketone, ester and lactones, respectively. The spectral changes in EPB and carbonyl index of all irradiated samples are shown in Figures 2 and 3, where PP & EPB showed higher concentration of photoproducts than other samples.

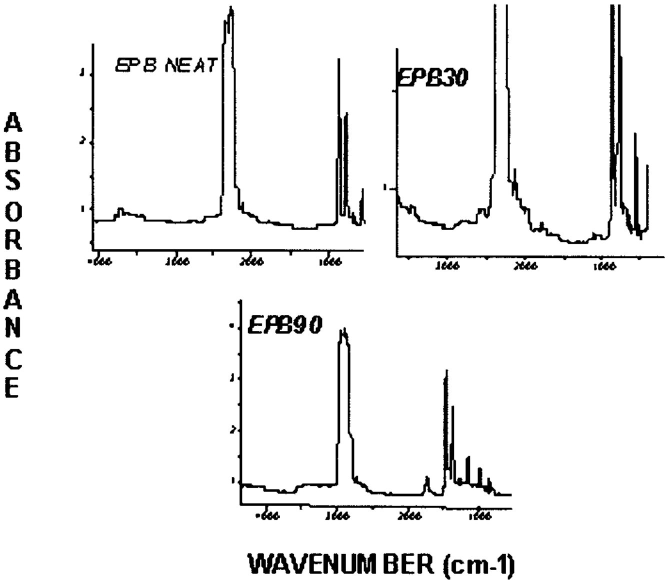

Figure 2. FT-IR spectral changes during UV exposure of EPB samples for 0-90 hrs

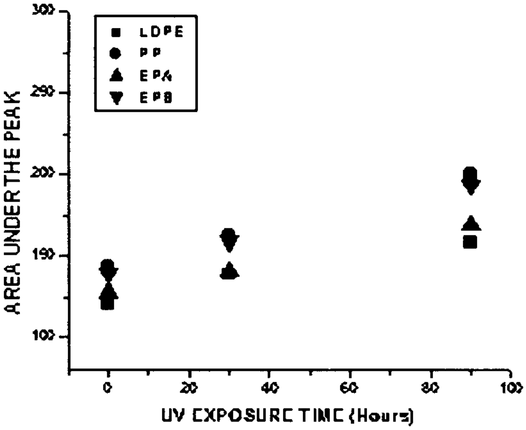

Figure 3. Carbonyl Index of UV irradiated samples

Figure 4 illustrates the comparative percent weight loss of irradiated and unirradiated polymers. It is clearly seen that compostability (weight loss) increased not only with irradiation time but also with the period of composting and temperature.

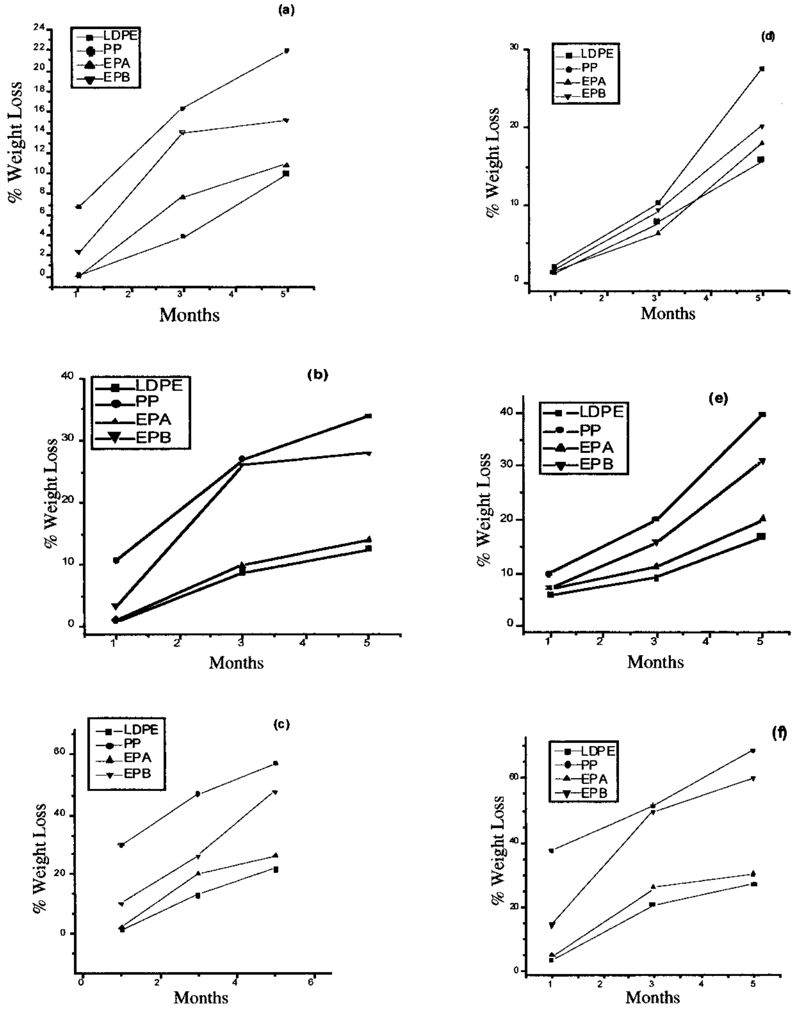

Figure 4. Weight loss in normal composting (a, b, c, for 0, 30, 90 hrs irradiated samples, respectively) and weight loss in accelerated composting (d, e, f, for 0, 30, 90 hrs irradiated samples, respectively)

It has been very well established that photodegradation of polyolefins increased the biodegradation.[11-14] We observed that photodegradation followed by thermal degradation in compost, rapidly enhanced the biodegradation of polyolefins and their copolymers. A further increase in the IR carbonyl region of PP and EPB was observed after 1 month accelerated composting with no detectable change in other part of spectra indicating thermal oxidation of samples. Further, the formation of primary alcohol in 90 hrs. irradiated EPB sample was indicated by the appearance of an absorption band at around 3390 cm^{-1} in FT-IR whereas, primary alcohol did not form upon NaOH treatment, suggesting that the primary alcohols generated by the oxidation of terminal methyl group, were not formed by ester hydrolysis as it was found in hydrocarbons.[15] Here, it must be noted that no leachable product was formed after 48 hr continuous stirring of UV irradiated samples in water at room temperature. Figure 5 depicted a detectable decrease in carbonyl hump with increase in unsaturation in the FT-IR spectra of 90 hrs irradiated and 5 month accelerated composted sample of EPB supporting the Albertsson[16-17] mechanism where it was concluded that this decrease is due to microbial consumption of the short chain carboxylic acids generated by hydrolysis of in chain esters.

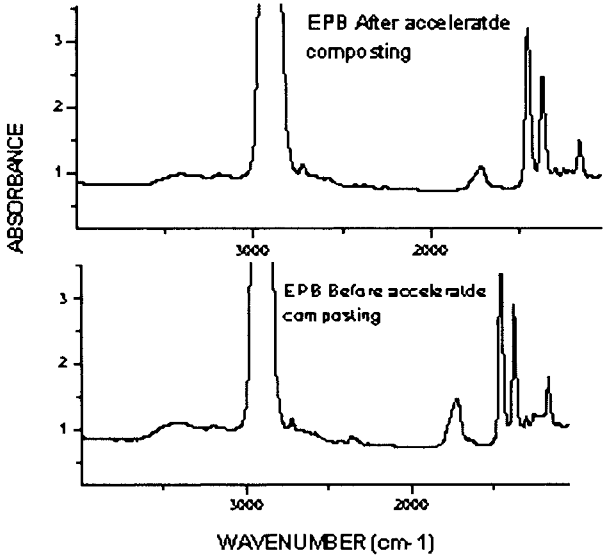

Figure 5. FT-IR spectra of 90 hrs irradiated and 5 month accelerated composted sample of EPB

The variation of $[\eta]$ of photo-oxidized and composted samples are shown in Table 1. where intrinsic viscosity increased with ethylene content and decreased with time of UV irradiation for all samples. The presence of any appreciable crosslinking was not observed in the present system, as samples remained completely soluble in decaline. A measurable increase in viscosity of 90 hrs irradiated samples, precisely, for PP and EPB copolymers after 3 months normal composting may be attributed to the preferable elimination of short chains during earlier microbial consumption. Such type of behavior was not observed in accelerated composting may be because of the continuous generation of short chains during thermal oxidation and $[\eta]$ decreased gradually. Thus, the fast biodegradation in accelerated composting was not only due to the higher concentration of functional group but also because of a longer number of short chains.

Amongst all unirradiated samples, PP and EPB showed higher compostability.

Table 1. $[\eta]$ changes during composting of samples.

$[\eta]$ Normal composting								
Months	LDPE		PP		EPA		EPB	
	0	90	0	90	0	90	0	90
Initial	3.42	0.889	1.197	0.189	3.31	0.812	2.51	0.537
1	3.41	0.874	1.189	0.164	3.29	0.796	2.46	0.519
3	3.36	0.863	1.173	0.132	3.21	0.779	2.34	0.492
5	3.27	0.847	1.153	0.101	3.11	0.748	2.25	0.465
$[\eta]$ Accelerated composting								
1	3.32	0.868	1.179	0.140	3.14	0.763	2.36	0.500
3	3.23	0.849	1.133	0.100	2.98	0.747	2.12	0.460
5	3.10	0.809	1.100	0.077	2.60	0.729	1.67	0.441

There was not significant difference in the weight loss of LDPE and EPA in both type of composting suggesting that there must be some threshold concentration of ethylene monomer in copolymer above which the compostability was not significantly affected. The 30 hrs. irradiated samples showed biodegradability in between 90 hrs irradiated. and unirradiated samples. The morphological changes were studied and crucial photographs of some interesting observations of degraded samples are highlighted in Figure 6. The surface changes of UV irradiated heterophasic copolymers have been studied in our earlier reports[10,18] where highly cracked network and deep eroded surface was found during the degradation of samples. It is evident from micrographs that there is much more surface deformation in 90 hrs irradiated PP and EPB. In 30 hrs irradiated samples such type of deformation or deepness of erosion was much less which is due to the presence of less oxidation products in comparison to longer irradiated samples and their more consumption by microbes, resulting in a good surface erosion in samples. The cavities on the surface were observed after composting of irradiated samples, suggesting that microorganisms penetrate the polymer matrix during the degradation process. The presence of small and large cavities on the surface may be due to the absence of uniform distribution of short branches or photodegradable products on the surface of specimens, which have been consumed by microbes as carbon source.

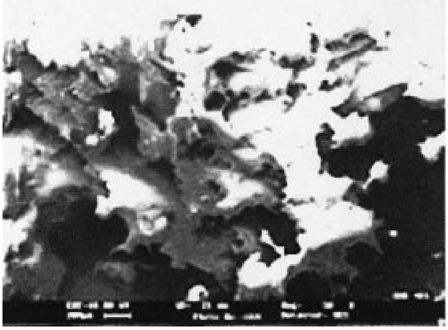

Figure 6 (a). 90 hrs Irradiated & composted EPA

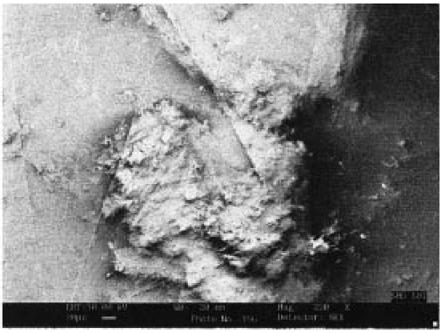

Figure 6 (b). 90 hrs Irradiated & composted EPB

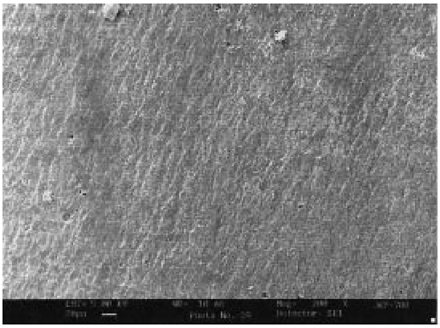

Figure 6 (c). 90 hrs Irradiated & composted PP

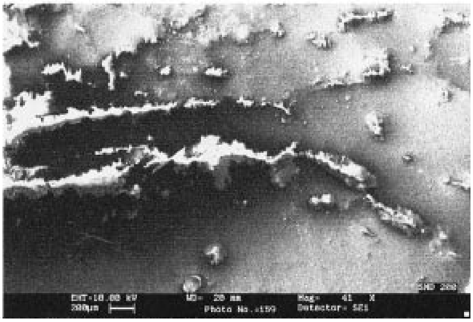

Figure 6 (d). 90 hrs Irradiated & composted LDPE

Conclusion

The hydroxyl and carbonyl indexes were increasing from 0-90 h UV irradiation for all samples. In general, a decrease in [η] and increase in chain scission was also observed with the irradiation and incubation time in compost whereas increase in [η] for earlier months of normal composting must be due to the short chain consumption by microbes. PP was more susceptible than LDPE to microbial attack in neat and irradiated samples. The higher weight losses in low viscosity samples and longer irradiated samples, suggested that chain scission and oxidized functional groups are important biodegradable units in the bio-degradation of polymers. The copolymer composition has an effect on biodegradability and it was observed from earlier study that there must be some threshold composition where ethylene/propylene ratio in copolymers does not affect the compostability.

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