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A New Additive Formulation to Improve Biodegradation of Low Density Polyethylene

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Abstract: Plastics waste management remains a major environmental issue due to over population and rapid economic development. The complete degradation of plastics mainly polyethylene remains a challenge and the current work is focused on enhancing the biodegradation of polyethylene. The photo degradation followed by biodegradation of Low density polyethylene (LDPE) could be enhanced by the use of Cobalt RLCD additives. The photo degraded film was subjected to biodegradation in the presence of the microbes such as *Bacillus licheniformis* isolated from a dump. The percentage of biodegradation of LDPE with 5% Cobalt RLCD additives was found to be 8.4% and 25.2% the direct biodegradation and the biodegradation of the photo degraded film respectively at the end of 90 days.

Keywords: Biodegradation, LDPE, Cobalt Ricinoleic Linoleate, Cinnamic Dextrose, ASTM D 5338.

Introduction

In highly populated cities the sight of overflowing garbage and unbearable stretch coming from it is a usual scenario. The solid waste generated at Chennai city in india alone is estimated to be 3200 tonnes per day of which 7% constitutes of plastic waste. Plastic broadly comprises of both thermoplastics and thermosetting plastics. The synthetic plastic industry has been one of the great industry successes in the last 70 years, transforming everyday life in a multiplicity of ways. The manufactures of thermoplastics convert light oil fractions which would otherwise be flared onto lightweight plastics. In essential, every life cycle analysis of plastics in comparison with other materials in e.g. packaging the use of plastic demonstrably leads to major savings in energy weight and pollution¹.

Polyethylene and polypropylene are the most commonly utilised high molecular weight thermoplastics. The usage of these plastics for packaging and for agricultural utilities is in an increasing order due to its remarkable mechanical properties. Polyethylene used mainly for packaging have very minimal usage time and exhibits a strong resistance to chemical, weather and biodegradation and remain accumulated as plastic waste in the environment²⁻⁴. The solution for this problem is still incomplete and lies in the development of biodegradable polymers, modification of polyethylene with biodegradable additives and enhancing the biodegradation of polyethylene by micro organisms. The environmental degradation of polyethylene is a very slow synergetic process consisting of initial photo and thermo- oxidation of polyethylene followed by biological activity of micro organisms. Photo oxidation involves the scission of the polyethylene chain resulting in generation of low molecular weight compounds⁵⁻⁷.

This approach offers several advantages, like diverse microbial inoculum or close relation to the real

conditions in the nature and in waste treatment processes. However, very few studies have been carried out under controlled conditions, i.e. experiments with well identified strains in the medium. As a part of our ongoing efforts in the development of degradable polyethylene⁷⁻⁹ we report an investigation aimed at microbial degradation study of photodegraded LDPE. Some Transition metal (Co, Mn and Fe) with some bio based natural oil (higher content of Fatty acid) exposure to natural UV radiation to improving polyolefin (LDPE and PP) degradation and some additive to improving photo and biodegradation of polyolefin¹⁰⁻³⁶. In this research work our new additive was exposed to natural UV, it has very shortly photodegradable compare to other literature studies¹⁻³⁷.

Material and methods

Cobalt (II) chloride hexahydrate purified, sodium hydroxide, Ricinoleic acid (12 -hydroxy oleic acid) from Castor oil, Linoleic acid from Sunflower oil, Cinnamic acid, Dextrose was used at 99% purification. LDPE purchased from Reliance pvt.ltd.

Synthesis of Cobalt (II) 11-9Z, 12Z-Octadeca-9, 12-dihydroxy-10,13 dihydroxyactadecaneate

Epoxy Ricinoleic acid from Ricinoleic acid

Hydrogen peroxide solution (30% in H₂O, 8.0 ml was added slowly into a stirred solution of the Ricinoleic acid (90%, 15 g) in formic acid (88% 14ml) at 4° C (ice bath). The reaction proceeded at room temperature with vigorous stirring (900 rpm) until the formation of a powdery solid was noticed in the reaction vessel (2-5h). The solid was collected via vacuum filtration, washed with H₂O (Chilled, 3x10 mL), and placed for 12 h under high vacuum to provide epoxidized Ricinoleic acid (ERA) as a white, powdery solid (14.7 g, 93%).

Cobalt ricinoleic linoleate (IUPAC - 11-((9Z, 12Z)-octadeca-9, 12- dienoyloxy)-10,13-dihydroxy ocat - decnoic acid)

To a mixture of ERA (31 g), 5g of P-toluene sulfonic acid (PTSA) and Toluene, Linoleic acid (6g) was added 15 h in order to keep the reaction mixture temperature under 70-80° C. The reaction mixture was subsequently heated to 90-100° C and refluxed for 3h. After reaction termination, the heating was stopped and the mixture was left to stand overnight at ambient room temperature. The mixture was washed with the water next day. The organic layer was dried over anhydrous Magnesium sulphate and the solvent was removed using the vacuum evaporator. The Cobalt RLCD additive was synthesized based on Ricinoleic Linoleic acid. The resulting sodium salt was subsequently treated with 1 mole of aqueous Cobalt (II) salt. The Cobalt Ricinoleic Linoleate obtained was washed and purified ethanol washing.

Synthesis of Cinnamic Dextrose

One Mole of Cinnamic acid with one mole of Dextrose reacted in the presence of hydrochloric acid as a catalyst to form Cinnamic dextrose ((E)-1-formyl-2,3,4,5-tetrahydroxypentyl cinnamate). The one mole of Cobalt Ricinoleic linoleate (RL) additive mixed with one mole of Cinnamic Dextrose in LDPE during processing for the film preparation. The Cobalt (RL) and Cinnamic Dextrose (CD) additive were characterized by using Perkin Elmer system 2000(USA) Fourier Transform Infrared Spectrometer (FTIR) to confirm functional group consist of the same additive and their chemical structure (Figure- 1(a, b)).

Blending and film preparation of LDPE

The Cobalt (RL) and Cinnamic Dextrose (CD) additive (Cobalt RLCD) as 1:1 ratio was melt blended with LDPE at 5wt% in (Haake, Rheomex OS, PTW16, Thermo scientific, Germany) Modular Torque Rheometer. The Modular Torque Rheometer blending was carried out at temperature range of 100-190 °C (from die to hopper) and a screw speed of 115-140 rpm. Subsequently, the pellets are dried in a dehumidifier at 70°C for two hours to remove moisture. The pellets produced were subsequently dried and subjected to film cast process to produce films of 50 μ thicknesses.

Photodegradation

All blended samples were subjected to photo degradation studies using the natural UV, the natural weathering for continues process for 24 hours day by day at 30°C. Humidity was 61 %, Power was 32 watt/m², 2nd -29th, July, 2011. Length 27.5 cm and 2.5 cm width were used to evaluate the degradation phenomenon (ASTM D 5208).

Fourier Transform Infrared Spectroscopy (FTIR)

The structural changes in LDPE films due to the presence of Cobalt Ricinoleic linoleate (Cobalt RL) and Cinnamic dextrose additive exposure to natural UV radiation were studied by Nicolet 67000 (USA) Fourier Transform Infrared Spectroscopy (FTIR) with the wave number range of 400-4000 cm^{-1} .

Scanning Electron Microscopic (SEM) Analysis

The scanning electron microscopic analysis of a fractured surface of LDPE films with Cobalt RLCD additive was carried out using the CARL ZESIS Model: EVO MA 15 scanning electron microscope. The surface of the samples was coated with conductive heavy metal such as gold.

Result and Discussion

Fourier Transforms Infrared Spectroscopy (FTIR)

The carbonyl groups are formed in LDPE with prooxidant bio active additive is degraded to short pieces though β -oxidation and glycolysis pathway. *Bacillus licheniformis* standard solid compost test was used in the degradation of LDPE with the prooxidant bioactive additive films.

Table 1. The characteristic peak value in the FTIR spectra for LDPE

IR Frequency (cm^{-1})	Band and Functional group
3399	O-H Stretching vibration
2958, 2849	C-H asymmetric and symmetric vibration
2657, 2657, 2344	O-H stretching (Carboxylic acid)
2019, 1897, 1714	C=O stretching vibration
1622	C=C stretching vibration
1463, 1472, 1411	CH_3 (alkane) bending vibration
1375	CH_2 (alkane) rocking vibration
1292	CH_2 (alkane) wagging vibration
1170	C-H bending vibration
1108	C-O alcohol, ester, ether

The FTIR spectra, after the biodegradation of LDPE with Co RLCD and the characteristic peak value are presented in Table 1, 2 and in Figure 1, 2. After the biodegraded film, the absorption band in the 1714 cm^{-1} region was attributed to C=O stretching vibrations of the ester group in LDPE with additives. This intensity changes due to enzymatic action and biochemical pathway of the biodegraded film. In the FTIR of LDPE after the biodegradation and the biodegradation of the photo degraded film at the end of 90 days. It is clearly seen that there are bands in three regions of the spectrum which have been changed in the range from 3600 to 3100 cm^{-1} and it appeared a wide peak which is due to the hydroxyl group during the cytosol enzymatic process. Further, the new absorption bands in the range from 1850 cm^{-1} to 1600 cm^{-1} was assigned to the carbonyl group (Arkatkar et al 2010; Wallstrom et al 2005). The carbonyl appearing during degradation is very useful to characterize the mechanism of biotic degradation.

As shown in (Figure- 1 & 2), ricinoleic acid is a naturally occurring unsaturated omega fatty acid and the additive synthesized is a derivative of ricinoleic acid Cobalt RLCD. These bio active additives were degraded by β -oxidation and glycolysis pathway.

β - Oxidation Pathway in Cytosol for Degradation of Polyolefin

The β -oxidation is a four-step, enzyme-mediated sequence of oxidation, hydrolysis, and thiolysis reactions that occur in all microbes. The β -oxidation occurs in cytosol where multiple enzymes act on the existing double bonds in the unsaturated fatty acid. The synthesized additive is a medium chained (<20) fatty acids and transport directly to the cytosol. The structure of LDPE is in a well organized manner and the initial structural cleavage is facilitated as a result of exposure of the films to UV/Sunlight. The size of photodegraded (abiotic) LDPE molecules are sufficient enough to pass through the cellular membrane. The transport of these molecules is the key step in initiating degradation (Albertsson et al 1987).

Figure 1: Comparison of the FTIR spectra of LDPE -5% Cobalt Ricinoleic linoleate cinnamic dextrose (Cobalt RLCD) additive, the biodegradation film (a) and the biodegradation of the photo degraded film (b)

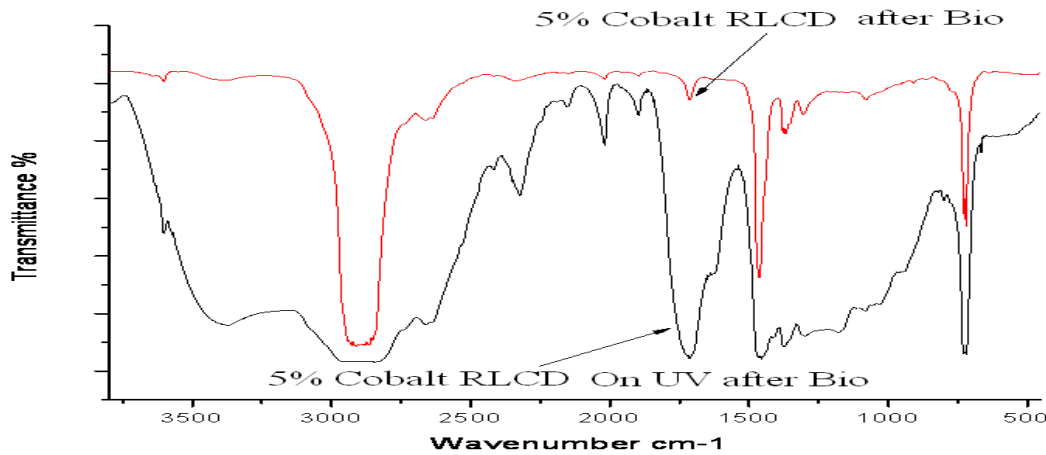
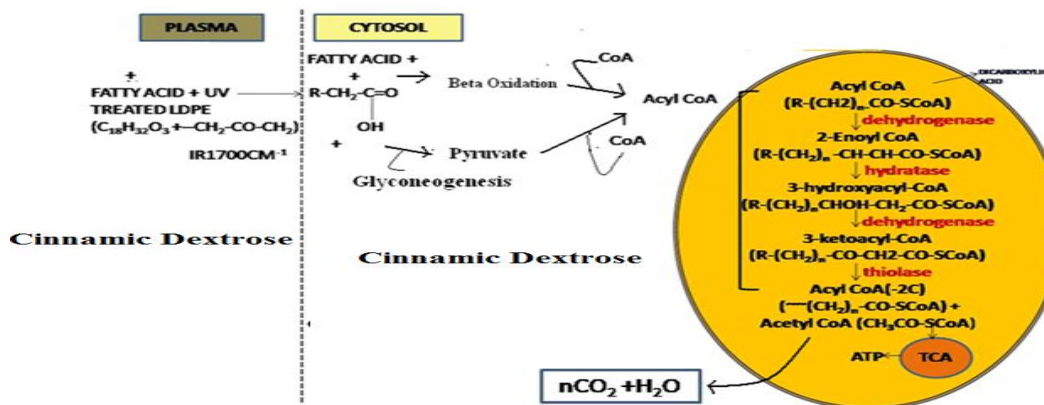


Figure 2: Biodegradation mechanism of Cobalt RLCD mixed with Polyethylene film



The synthesized bio active additive mixed easily with the LDPE, LDPE molecule and pretreatment after UV sunlight results in photodegradation and thus depolymerised and membrane transport becomes possible. The fatty acids contained in the additive along with the mixed polymers are first activated by an Acyl-coenzyme A synthetase utilizing ATP for the production of a reactive fatty Acyl adenylate that further reacts with coenzyme A and forms fatty acyl-CoA. There is different Acyl-coenzyme A synthetase for the different lengths of fatty acids. The synthesized additive contains short chain fatty acids is capable of diffusing directly into cytosol and are then activated by Acyl-coenzyme A synthetase in the cytosol. In the first step of the beta-oxidation cycle, a double bond between C-2 and C-3 is formed, producing a trans-Δ²-enoyl-CoA. This is catalyzed by Acyl-CoA-dehydrogenase in the cytosol, which have forms specific to the different lengths of fatty acids. In the second step, enoyl CoA hydratase hydrates the newly formed double bond between C-2 and C-3, producing an L-beta-hydroxyacyl CoA. Next, L-beta-hydroxyacyl CoA dehydrogenase converts the hydroxyl group into a keto group, producing a beta-ketoacyl CoA. In the third and final step, the enzyme beta-ketothiolase cleaves the β-ketoacyl CoA and inserts the thiol group of another CoA between C-2 and C-3, reducing the acyl-CoA by 2 carbons and generating acetyl-CoA. The final two steps also have enzymatic forms specific to short chain fatty acids. This four step cycle repeats removing 2 carbons from the fatty acid each time until it becomes acetyl-CoA. Acetyl-CoA is necessary for the citric acid cycle, among other cellular processes. Thus it's apparent that even small amounts of this additive are capable of initiating a significant rate of biodegradation.

Glycogenesis Pathway in Cytosol for Degradation of Polyethylene

The unsaturated dextrose additives such as Cobalt RLCD additives with LDPE after the biotic exposure and the biotic exposure of the photodegraded film at the end of 90 days in soil burial and standard solid compost treatment.

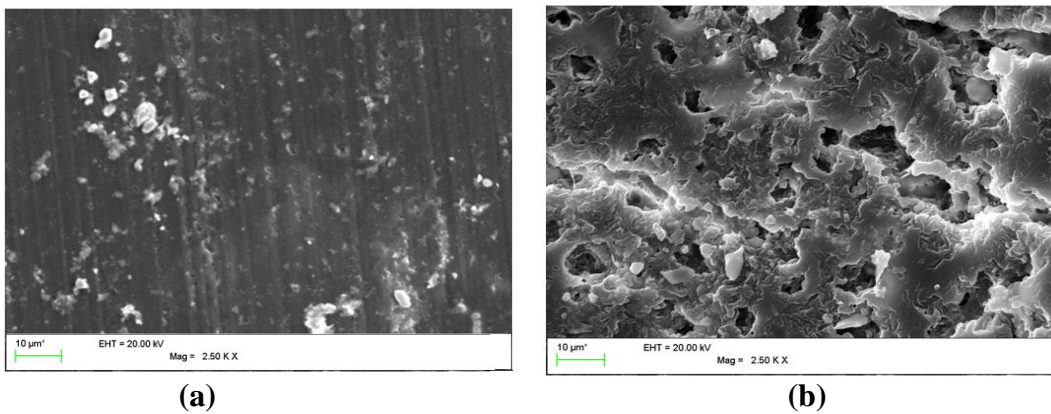
The unsaturated dextrose (cinnamic dextrose) additives metabolism is the glycolytic or Embden-Meyerhof-pathway and the second is the Krebs cycle (also called the citric acid or tricarboxylic acid cycle) and third is the series of membrane-bound electron transport oxidations coupled to oxidative phosphorylation. Respiration takes place when the unsaturated dextrose is oxidized shorter ageing and completely to CO₂ and H₂O. In aerobic respiration, molecular O₂ serves as the terminal acceptor of electrons (Chapter 1).

The fragmentation of the LDPE molecules is very much visible where in complete utilization of the additive as energy source for the growth of the microorganism is evident.

Scanning Electron Microscopy (SEM)

The surface topography and microbial colonization of virgin LDPE and film with additive exposed to UV/Sunlight and then standard solid compost experiments for 90 days were studied using scanning electron microscopy at a magnification of 2.00 KX. LDPE films with additive exposed to UV/sunlight for specified period were subjected to standard municipal solid compost for 90 days. The surface of the biodegradation of LDPE films are shown in (Figure- 3 (a)) it is clearly seen there are very few area changes on the surface. In case of LDPE biodegradation of the photo degraded film there was a clear visualization of pores on the surface of the film as shown in (Figure- 3(b)).

Figure 3 (a,b): LDPE- 5% Cobalt RLCD additives after biodegradation film (a), LDPE with Cobalt RLCD additive of the biodegradation of the photo degraded film (b).



Percentage of Biodegradation as per ASTMD 5338

As shown in (Figure- 4(a,b)), the LDPE films with additives, the direct biodegradation and the biodegradation of the photo degraded film by standard composting test method as per ASTM 5338 shows 8.4% and 25.2% biodegradation respectively for a period of 90 days.

Figure 4 (a, b): The percentage of biodegradation, the biodegradation film (a) and the biodegradation of the photo degraded film (b)

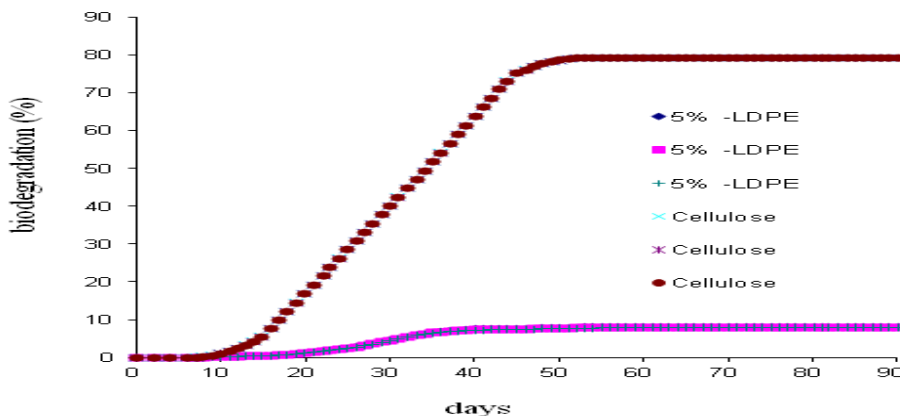


Fig. 4(a)

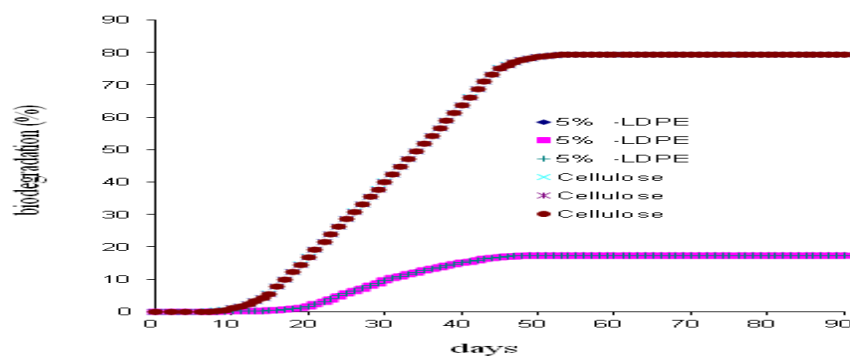


Fig.4 (b)

Conclusion

Based on these results it can be concluded that Cobalt Ricinoleic Linoleate mixed with cinnamic dextrose additives (Cobalt RLCD) promoted the biodegradation of LDPE. The LDPE films with additives, the direct biodegradation and the biodegradation of the photo degraded film by standard composting test method as per ASTM 5338 shows 8.0% and 24% biodegradation respectively for a period of 90 days.

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