



Chemical Methodologies

Journal homepage: <http://chemmethod.com>



Original Research article

Structural Characteristics Changes after the Degradation of Polyethylene with Cobalt 12-Hydroxy Oleate Acrylic Dextrose

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ARTICLE INFORMATION

Received: 07 June 2018

Received in revised: 27 August 2018

Accepted: 12 September 2018

Available online: 12 September 2018

DOI:

[10.22034/CHEMM.2018.135055.1062](https://doi.org/10.22034/CHEMM.2018.135055.1062)

KEYWORDS

LDPE

Biodegradation

Photooxidation

Cobalt ricinoleate (12-hydroxy) with acrylic dextrose (CRAD)

ABSTRACT

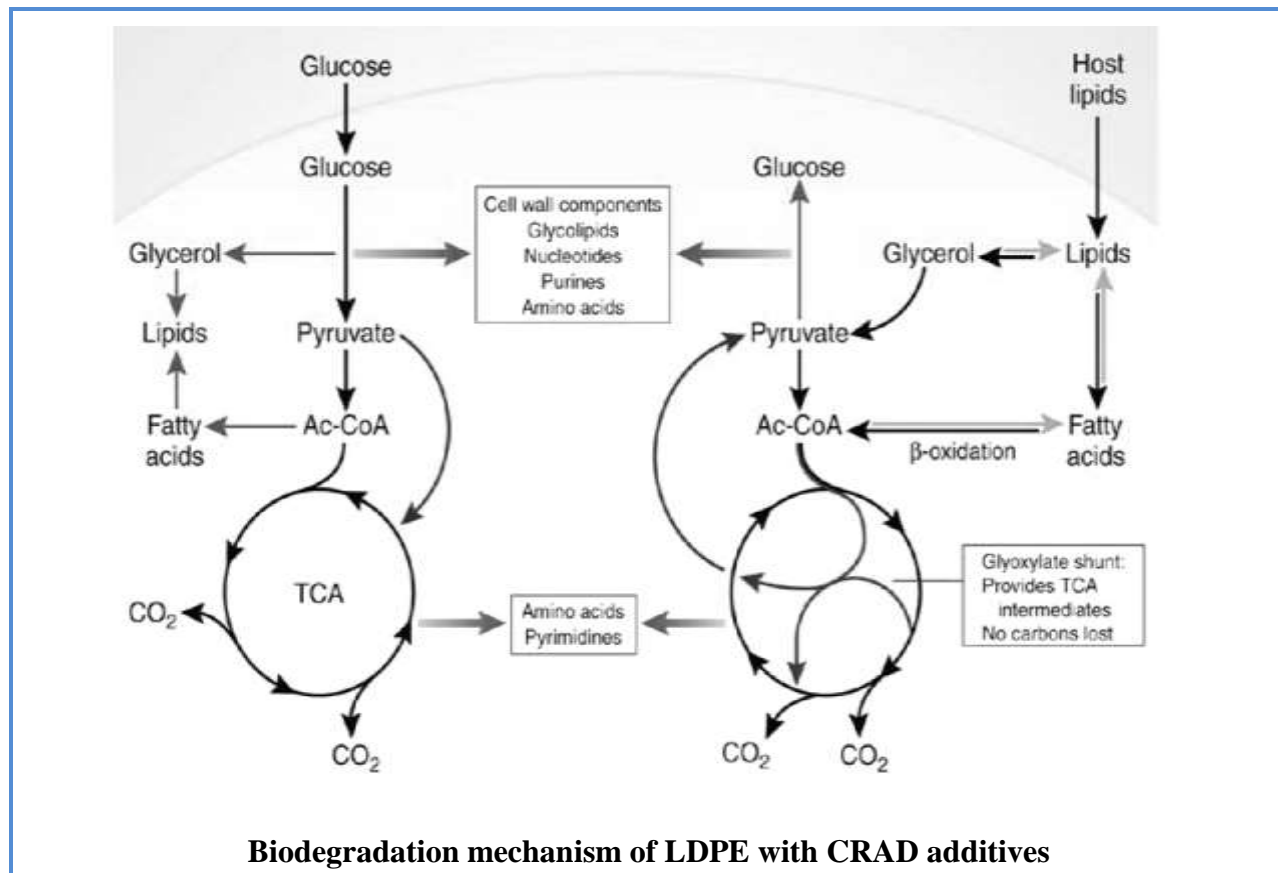
The novel bio-based additives synthesized in the present research were incorporated into LDPE, LDPE in about 1-5 wt % subsequently processed to produce films of 50 μ thickness. The bio-based additive such as cobalt ricinoleate (12-hydroxy) with acrylic dextrose (CRAD) additives was successfully synthesized and their performance on the photo and biodegradability of polyethylene films were studied under the influence of accelerated UV/sunlight. The changes in the structural of polymer due degradation were investigated by the FTIR. The percentage of biodegradation of the photodegraded film was analyzed by ASTM D 5338-98. The photodegraded film was subjected to biodegradation in the presence of *Bacillus licheniformis* isolated from a dump. The percentage of biodegradation is 30%.

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Graphical Abstract



Introduction

Plastics waste management has been assigned as a major environmental issue due to overpopulation and rapid economic development [1]. Exposure to ultra violet radiation may cause significant degradation of many materials [2]. UV radiation causes photooxidative degradation which results in breaking the polymer chains [3-11], produces radical and reduces the molecular weight, causing deterioration of mechanical properties and leading to useless material, after an unpredictable time [11-17]. Polystyrene (PS), one of the most important materials from the modern plastic industry, has been used all over the world, due to its excellent physical properties and low-cost [18-23]. When polystyrene is subjected to UV irradiation in the presence of air, it undergoes a rapid yellowing and a gradual embrittlement [23-26].

The complete degradation of plastics mainly polyethylene remains a challenge and the current work is focused on enhancing the biodegradation of polyethylene. The photodegradation followed by biodegradation of PE and PP could be enhanced by the use of bio-based additives.

Experimental

Material and methods

Cobaltous chloride hexahydrate purified, sodium hydroxide and ricinoleic acid (12-hydroxy oleic acid) were used without further purification. General purpose film grade LDPE has been used to prepare films. Milli-Q ultrapure water was used throughout the course of this work and acrylic dextrose were used [26].

Synthesis of cobalt 12-hydroxyoleate and acrylic dextrose

One mole of sodium hydroxide (NaOH) was mixed with 1000 mL of ethanol in a volumetric flask to get 1N NaOH solution. About 720 mL of 1N NaOH and 80 mL of castor oil (source for 12-hydroxy oleic acid) were taken in a round bottomed flask fitted with a condenser and refluxed for one hour. The contents in the flask were neutralized with 1N hydrochloric acid and washed with water. About 60 g of sodium salt of 12-hydroxy oleic acid was obtained. The resulting sodium salt was subsequently treated with 1 mole of aqueous cobalt (II) chloride hexahydrate salt. The cobalt ricinoleate (12-hydroxyoleate) obtained was washed and finally dried by passing over anhydrous sodium sulphate [26].

One mole of acrylic acid with one mole of dextrose in the presence of concentrated hydrochloric acid as a catalyst to produce acrylic dextrose was synthesized. Cobalt ricinoleate (12-hydroxyoleate) acrylic dextrose (CRAD) was mixed with LDPE film.

Blending and film preparation of LDPE

The cobalt 12-hydroxyoleate mixed with acrylic dextrose was melt and, then, blended with LDPE at three different formulations 1, 3 & 5% respectively 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) & a screw speed of 100 rpm. Subsequently, the pellets are dried in a dehumidifier at 70 °C for two hours to remove moisture. The pellets produced were subsequently dried & subjected to film cast process to produce films of 50 μ thicknesses.

Photodegradation

All blended samples were subjected to photodegradation studies using QUV UV Weather-o-meter.

Fourier Transform Infrared Spectroscopy (FTIR)

The structural changes in LDPE films due to the presence of cobalt ricinoleate acrylic dextrose (CRAD) additive exposure to UV radiation were studied by Nicolet 6000 (USA) Fourier Transform Infrared Spectroscopy (FTIR) with the wave number range of 400-4000 cm^{-1} .

Titration method of CO₂ determined test (ASTM D 5338)

The details of the biodegradation experiment are summarized below;

Sample detail: Before and after brittle fragmented photodegraded LDPE-CRAD additives.

Conditions of reaction mixtures

Origin of compost	: Municipal and vegetable waste
Reaction Temperature	: 58 °C
Dry Solid (%)	: 52%
Volatile Solid (%)	: 20
Air flow rate	: 100 mL/min
Test duration (day)	: 90 days
PH	: 7.4
Reference material	: Cellulose
Volume of reaction vessel	: 3000 mL

The preparation and ageing of the compost for biodegradation of film samples were carried out as per the standard. The PH value for all the samples, control and blank, was maintained. Barium hydroxide solution (0.024 N) was prepared by dissolving 4.0 g of anhydrous barium hydroxide in 1000 mL of distilled water. The solution was filtered and the normality was determined by titrating against standard acid solution and stored in a sealed container as a clear solution to prevent absorption of CO₂ from air. About 5-20 L of 0.024 N barium hydroxide solutions was prepared at a time for running a series of tests. However, care was taken that a film of BaCO₃ does not form on the surface of the solution in the glass vessels, which would inhibit CO₂ diffusion into the absorbing medium.

Procedure: The composting vessels were incubated in diffuse light minimum for a period of 90 days & the temperature of the system was maintained at 58±2 °C. The CO₂ & O₂ concentrations were checked in the outgoing air daily with a minimum time interval of 6 hrs after the first week. The air flow was adjusted to maintain a CO₂ concentration of at least 2% volume to allow accurate determination of CO₂ level in the exhaust air. Composting vessels were shaken weekly to prevent

extensive channeling which could provide uniform attack of microbes on test specimen and provide an even distribution of moisture. The incubation time was fixed for 90 days.

Carbon dioxide analysis

The carbon dioxide (CO₂) produced in each vessel reacted with Ba(OH)₂ and was precipitated as barium carbonate (BaCO₃). The amount of the produced carbon dioxide was determined by titrating the remaining barium hydroxide with 0.05 N hydrochloric acid to a phenolphthalein end point. Because of the static incubation, the barium carbonate built up on the surface of the liquid was periodically broken up by shaking the vessel gently to ensure the continued absorption of the evolved carbon dioxide. The hydroxide traps were removed and titrated before their capacity exceeded. At the time of removal of the traps, the vessel was weighed to monitor moisture loss from the soil and allowed to sit open so that the air was refreshed before replacing fresh barium hydroxide and releasing the vessel. The carbon dioxide evolution rate reaches a plateau when all of the accessible carbon is oxidized. The test was terminated at this point. At the conclusion of the test, the pH and moisture and ash content of the soil is measured and recorded.

Result and Discussion

FTIR characterization of LDPE-CRAD

The chemical changes took place in the polyethylene films due to photo-oxidation, the evolution of the FTIR spectra was studied with respect to exposure time, similar changes in the FTIR spectra were observed in all the samples, the extent of change depends on the concentration additives. Some new features show the increased intensity after UV exposure. A new band appears around 1712-1720 cm⁻¹ which can be attributed to the generation of carbonyl groups primarily on the surface of the polymer. The increases in the absorbance of these bands were, however, more pronounced for samples containing CRAD additives than neat LDPE. As far as the band shape is concerned, a progressive broadening of the carbonyl band was observed. The carbonyl band is a result of overlapping of absorption bands due to several functional groups like ketones, carboxylic acids, aldehydes, esters and peroxy-carboxylic acids, etc. It can be seen from the Figures 1 and 2 which the absorption intensity increases with increasing the concentration of the additive from 1% to 5%.

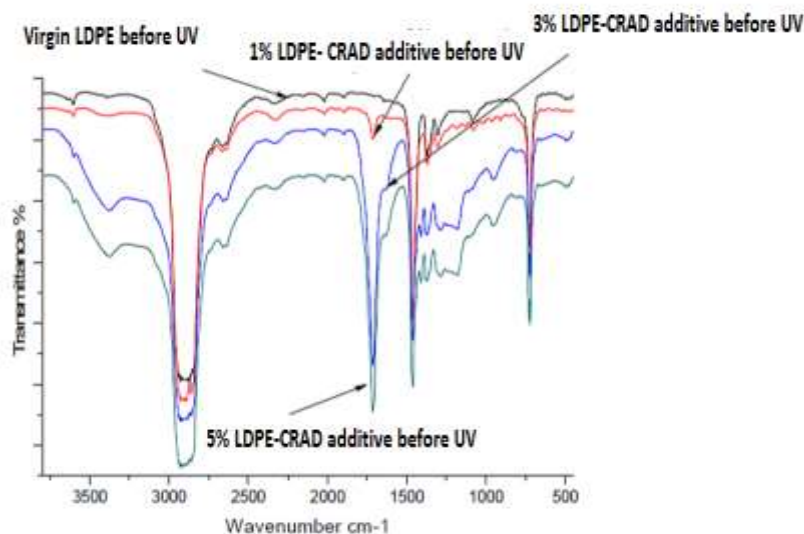


Figure 1. The FTIR peak of LDPE with CRAD before UV exposure

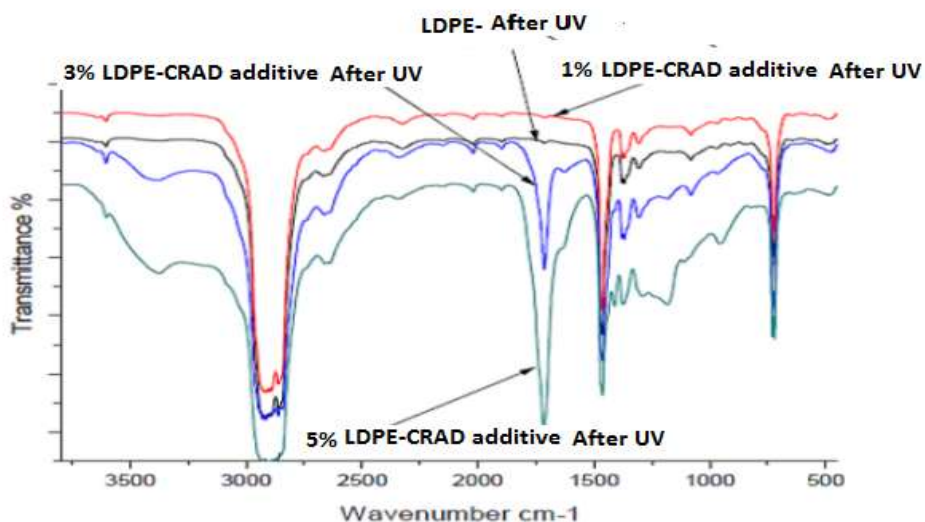


Figure 2. The FTIR peak of LDPE with CRAD after UV exposure for 50 hours

The carbonyl groups are formed in LDPE with CRAD additive which is degraded to short pieces through β -oxidation and glycolysis pathway. The *Bacillus licheniformis* standard solid compost test was used in the degradation of LDPE, CRAD additive films. The FTIR spectra, before and after the biotic exposure of LDPE with CRAD and the characteristic peak value are Figure 3. The FTIR spectra of the biotic exposed film shows a significantly lower absorption intensity of C=O and O-C-C bands when compared to that of film before the biotic exposure film. After the biotic exposed 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 biotic exposure film. In the FTIR of LDPE after the biotic exposure and the biotic exposure of the photodegraded film at the end of 90 days. It is clearly see 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 hydroxy group during the cytosol enzymatic process. Further, the new absorbtion bands in the range from 1850 cm^{-1} to 1600 cm^{-1} was assigned to the carbonyl group. The carbonyl appearing during degradation is very useful to characterize the mechanism of biotic degradation.

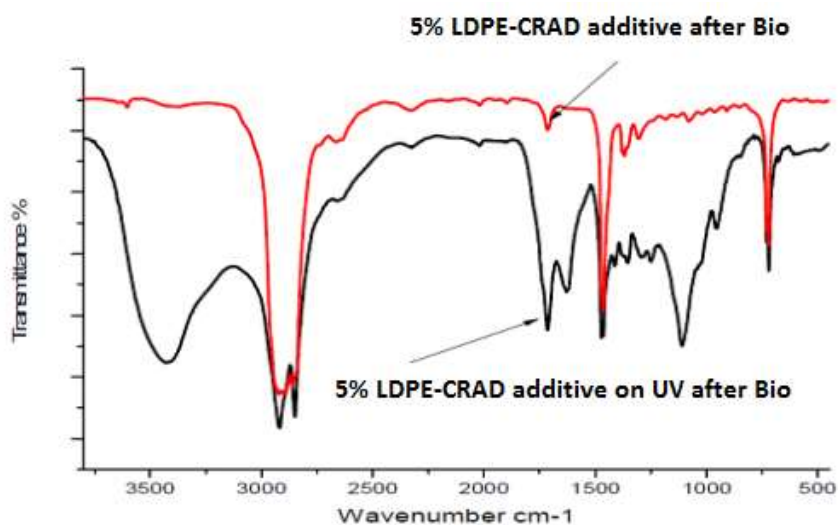


Figure 3. The FTIR peak of LDPE with CRAD on UV after bio

Biodegradation of the LDPE with CRAD additives

As shown in Figure 4. conditions of reaction mixtures: Organ of compost; livestock excrement, municipal and Vegetable waste which applied the method were used for the determination of the biodegradability of the polyethylene which was based on the International Standard (*ASTM D 5338-98*). Moreover, it measures the evolved CO_2 amount from both the blank vessel without a sample and the sample vessel including a 10 g LDPE with CRAD samples. According to ASTM D 5338 test procedure, fragments progressively occur in the biodegradation of the photodegraded films. Moreover, the biodegradation test results reveal that the LDPE-CRAD additives show 30% of biodegradation on photodegraded LDPE films when observed at the end of 90 days.

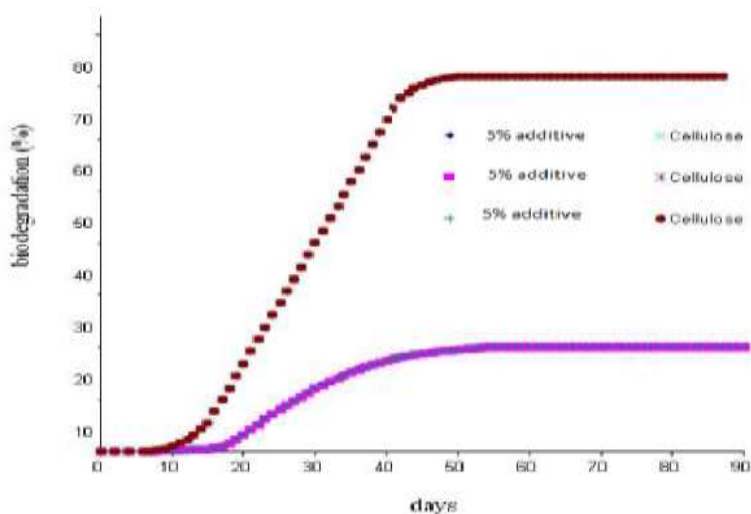


Figure 4. The percentage of biodegradation of LDPE with 5% CRAD additives as per ASTM D 5338

β -Oxidation pathway and glycogenesis process in cytosol for degradation of LDPE

As shown in Figure 5, ricinoleic acid is a naturally occurring unsaturated omega fatty acid and the synthesized additive is a derivative of ricinoleic acid such as cobalt 12-hydroxyl oleate acrylic dextrose. These bioactive additives were degraded by β -oxidation and glycogenesis pathway. 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, LLDPE and PP 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, LLDPE and PP molecules is sufficient enough to pass through the cellular membrane. The transport of these molecules is the key step in initiating degradation. The synthesized bioactive additive mixed easily with the LDPE, LLDPE, LLDPE/LDPE and PP molecule and pretreatment after UV sunlight results in photodegradation and thus are 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 further reacts with coenzyme A and forms fatty acyl-CoA. There is a different Acyl-coenzyme a synthetase for the different lengths of fatty acids. The synthesized additive which contains short chain fatty acids—which are, then, activated by Acyl-coenzyme A synthetase in the cytosol is capable of directly diffusing into cytosol. In the first step of the beta-oxidation cycle, a double bond between C-2 and C-3 is formed, producing a trans 2-enoyl-CoA. This is catalyzed by Acyl-CoA-dehydrogenase in the

cytosol, which has specific forms in accordance 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 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 is apparent that even small amounts of this additive is capable of initiating a significant rate of biodegradation.

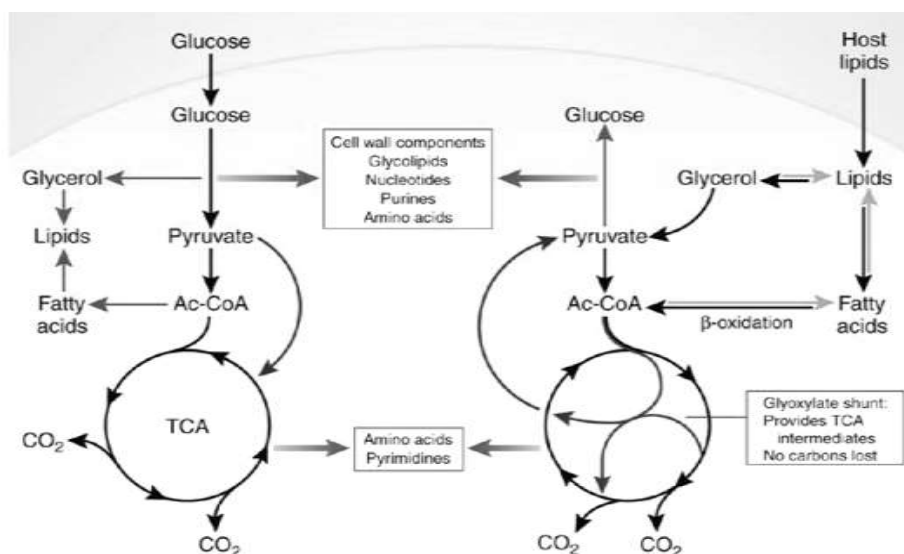


Figure 5. The biodegradation mechanism of LDPE with CRAD additives

The unsaturated dextrose additives of 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 (acrylic 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. 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.

Conclusion

LDPE with CRAD additive shows improvement in photodegradation rates. The extent of photodegradation is directly proportional to the concentration of the CRAD additive. After the UV exposure of films with additives for the specified period, the FTIR results show that a higher concentration of carbonyl and hydroxy groups were formed indicating the films which were degraded to a larger extent when compared to virgin films without additives. After the photodegradation was subjected to biodegradation, the FT-IR characteristic peak has been changed due to the β -oxidation and glycogenesis process.

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How to cite this manuscript: A. Umapathi Santhoskumar, N. Jaya Chitra. Structural Characteristics Changes After the Degradation of Polyethylene with Cobalt 12-Hydroxyoleate Acrylic Dextrose. *Chemical Methodologies* 3(1), 2019, 83-93. DOI: [10.22034/CHEMM.2018.135055.1062](https://doi.org/10.22034/CHEMM.2018.135055.1062).