



Performance Evaluation of Photo and Biodegradation of Low Density Polyethylene Using Photodegradable Additive 4, 4' Bis (Dimethylamino) Benzophenone (DMDAB) [Part – I]

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Authors' contributions

This work was carried out in collaboration between all authors. Author AKN designed the study, set-up the experiment, performed the statistical analysis, wrote the first draft and finalized the manuscript. Author RV managed the literature searches and scientific information related to this work, performed the experiments, and collected the data and participated in writing the first draft. Author AKSB worked on the revision of the manuscript and supported the work in all steps. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

The additive 4, 4' Bis (Dimethylamino) Benzophenone (DMDAB) is used as a photodegradable additive, which is commercially available and reported as UV active. DMDAB was melt blended with LDPE at three different formulations 1, 3 & 5 (w/w) % respectively in twin screw extruder. After blending with LDPE the performance of photo and bio degradation was evaluated. The films were evaluated for their mechanical, thermal, infrared spectroscopic analysis, and morphological characteristics. The results show that DMDAB can be used, as an effective photodegradable additive. The photo degradation rate of the additive is very high at lower concentration of DMDAB additive and the biodegradation was also proving that some low molecular weight species was formed during photo degradation, which is responsible for the 16% biodegradation after 50 days.

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1. INTRODUCTION

Products made from plastics, especially polyolefins, have increased significantly in recent decades largely due to their low cost, good mechanical properties, light weight and durability. These properties that make plastics the material of choice for many applications, particularly for single use packaging, together with an increase in usage have also created disposal problems at the end of the useful life of these products. Traditional disposal methods include recycling, incineration and burying in landfill. The aim of degradable polyolefin design is to retain functionality as a commodity plastic for the required service life but degrade to non-toxic end products in a disposal environment.

Degradable polyolefin systems are typically designed to oxo-degrade undergoing changes in chemical structure as a result of oxidation in air, causing the breakdown of the molecules into small fragments that are then bioassimilated. In the first stage of oxo-biodegradation, the oxidative degradation of the polymer can be accelerated by ultraviolet (UV) light (photo degradation) or by thermal degradation using heat over time. The hydro peroxide group ($-CH-OOH$) is the primary oxidation product of the photo degradation of polyethylene [1] and is both thermally and photolytically unstable. It decomposes to produce two radicals, each of which can participate in a chain reaction process.

The presence of carbonyl groups in a degraded polymer indicates that oxidation has taken place and also means that the material is vulnerable to further degradation since these groups are photo labile [2]. The ketones that are introduced onto the polymer backbone by photo-oxidation can undergo Norrish I and/or Norrish II degradation [2]. The rate of thermal degradation directly depends upon the temperature, with higher values achievable at higher temperatures [3]. The influence of mechanical forces on photo degradation has also been reported with stress shown to accelerate photo degradation [5].

The second stage is the biodegradation of the oxidation products by microorganisms (bacteria, fungi and algae) that consume the oxidized carbon backbone fragments to form CO_2 , H_2O and biomass. It has been reported that to achieve significant biodegradation in a reasonable time period, the average molecular weight of oxidized polyolefin should be less than 5000 Da [6].

Although polyolefins such as PE and PP will eventually degrade naturally, the process is usually long and can span over many decades. A possible solution is to use an additive (prodegradant) capable of accelerating the reaction of the plastic with atmospheric oxygen and incorporating oxygen atoms into the polyolefin chains. Transition metal ions (iron, cobalt and manganese) are the most widely reported prodegradant additives. The attractiveness of these additives lies in their ability to catalyze the decomposition of hydro peroxides into free radicals [4]. The metal ions are generally introduced at trace levels in the form of transition metal salts of fatty acid esters, amides and dithiocarbamates. Gain Mark Technology [7] describes the use of fatty acid amides to improve the rate of the degradation of prodegradant systems containing transition metal ions. Benzophenone additives have also been reported together with ferrocene in the patents DE2244800 [8] and SU626101 [9]. The patent WO200259195 [10] describes a complex mixture of ferrocene with other metal ions as well as nonmetallic fillers.

The UV stabilizing effect of ZnO in polyolefins is well recognized [11-12] the control of photo activity via the introduction of metal ions into the lattice has also been reported [13 – 14]. Similarly, the effect of transition metal doped TiO₂ on the photo degradation of polyethylene has recently been reported [15].

Most commercial polyolefins will undergo chemical modifications under UV light because they contain impurities or additives that possess chromophoric groups such as carbonyl groups and conjugated double bonds, they have absorption maxima between 200 and 300nm [2]. The introduction of these groups (Such as Ketone copolymers, 1, 2-Oxo-hydroxy groups [16], Unsaturated alcohols or esters [17], Benzophenones [18], γ -Pyrones [19], β -Diketones [20], Polyisobutylene [21], Selected amines [22]) into the polymer accelerate the photo degradation.

Commercially available, TDPA technology utilizes a combination of transition metal carboxylate and an aliphatic poly(hydroxyl-carboxyl acid) in a polyolefin, as disclosed in US patent 5854304 [23]. Metal carboxylates are well known to accelerate the per oxidation of hydrocarbon polymers [24]. The preferred metal carboxylates are cerium, cobalt and iron stearate. Iron is recognized as photo-initiating where as cobalt (nickel, chromium (IV) and copper) are sensitive to thermal activation [25]. Biodegradation (i.e. mineralization) of LDPE containing TDPA was further studied in controlled laboratory environments [26].

Benzophenone based additives are known to accelerate the degradation of polymers in the presence of air and UV light. US patent 4038227 describes the use of benzophenone and anthraquinone additives as prodegradants in PE and gives examples of activity both alone and together with other additives such as iron stearate and colored pigments [27]. The patent US3846395 (assigned to ICI) also discloses the use of benzophenones to degrade polyolefins [28]. In this patent the preferred additives are plaurylacetophenone and p-laurylbenzophenone. Benzophenones are also mentioned in the Japanese patent JP48070755 [29] where they are used together with transition metal compounds and in the patent WO9211298 [30] which disclose the use of two transition metal compounds, iron and copper stearate and benzophenone. The US patent US4024324 describes the use of aryl ketones together with a borate or phosphate ester of an alkanolamine for greater control of strength prior to degradation [31].

The additive 4, 4' Bis (Dimethylamino) Benzophenone (DMDAB) is also a commercially available photodegradable additive, which is reported as UV active. The aim of this work is to evaluate the photo and biodegradation of low density polyethylene blended with DMDAB at three different formulations 1, 3 & 5% respectively in twin screw extruder. The films were evaluated for their mechanical, optical, thermal, infrared spectroscopic analysis, and morphological characteristics.

2. MATERIALS

2.1 Low Density Polyethylene (LDPE)

Low-density polyethylene was purchased from Reliance petro chemicals and used without further purification. The homo polymer LDPE (grade 24FS040) has a melt flow index of 2.4g/10 min.

2.2 4, 4' Bis (Dimethylamino) Benzophenone (DMDAB)

DMDAB used as a photo degradable additive, which is commercially available. DMDAB AR Grade with 98% purity obtained from Aldrich Polymer Products, USA has the melting point 174-176°C. The structural formula of DMDAB is given in Figure 1

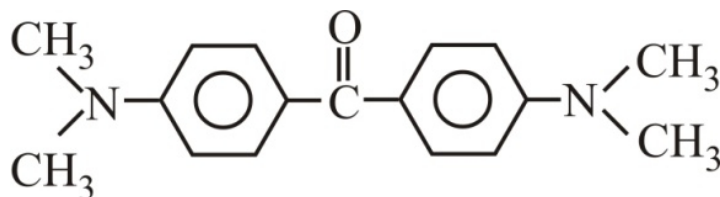


Figure 1. Structural Formula of 4, 4' Bis (Dimethylamino) Benzophenone (DMDAB)

The additive DMDAB is reported as UV active and giving absorption peak of 360 nm at 8×10^{-3} mol/l. DMDAB when mixed with polymer is capable of degrading polymer because this additive is photodegradable, active above $\lambda > 300$ nm and UV exposure was also done on the same UV range. The absorption peak of DMDAB is given in Figure 2.

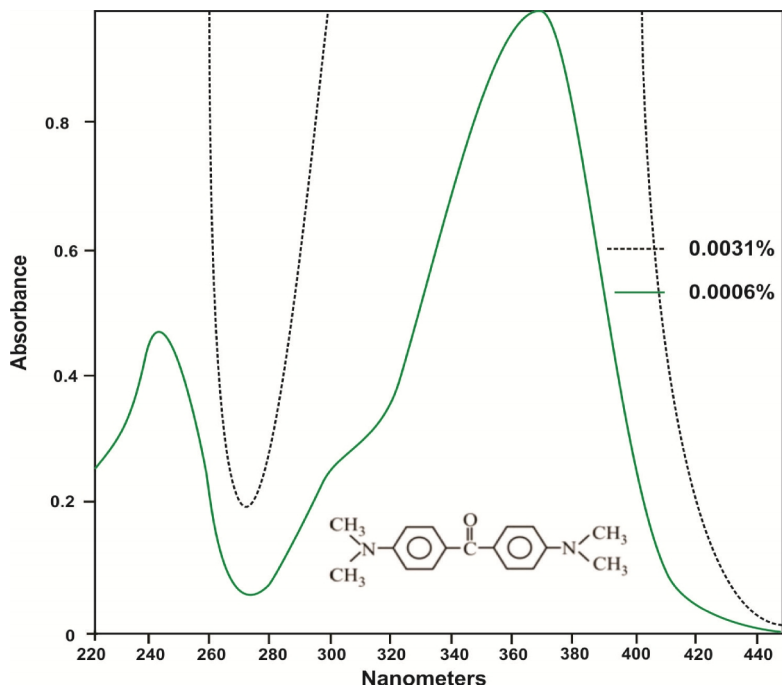


Figure 2. UV absorption spectra for 4, 4' Bis (Dimethylamino) Benzophenone (DMDAB)

3. PROCESSING AND TESTING WITH DMDAB-LDPE FILM

3.1 Twin Screw Extruder

The twin-screw extruder manufactured by M/s Berstorff, Germany used for the blending of the additive with the polymer. The extruder is having two co-rotating screw with 25mm screw dia and L/D ratio 48:1. The detailed specification for twin-screw extruder is given in Table 1.

Table 1. Technical Data of Twin Screw Extruder

| Technical Details | Parameters |
|----------------------|------------|
| Extruder Model | ZE 25 |
| Core dia | 17 mm |
| Torque | 6 NM |
| Rated torque / shaft | 0.58 NM |

DMDAB was melt blended with LDPE at 3 different formulations 1, 3 & 5% respectively in twin screw extruder. The pellets produced were subsequently dried & subjected to film blowing process to produce films of 50 microns thickness. The aforementioned films were subjected to photo- degradation studies as per the method given in 3.2

3.2 Photo Degradation

All the blended samples were subjected to photo- degradation studies as per ASTM D 5208 using ATLAS UV Weather-o-meter. Films of 25 mm width were used to evaluate the degradation phenomenon. Samples were exposed to two different test cycles of UV irradiation & condensation (condensation means water sprinkler phase as per ASTM D 5208 to simulate the actual condition of day & night.) & subsequently tested & characterized at 1, 2, 4 & 6 days interval time. The cycle time is given in the Table 2.

Table 2. UV cycle for photo degradation studies

| S. No | Cycle | Irradiation W/m ² | Temperature °C | Time Hrs |
|-------|----------------|------------------------------|-------------------|----------|
| 1. | UV Irradiation | 0.63 | 60 ⁰ C | 8 |
| 2. | Condensation | - | 50 ⁰ C | 4 |

In a test for 24 hours, first eight hours is UV cycle and the next four hours is condensation cycle. For the remaining time the cycle was repeated in the same order.

3.3 Mechanical Properties

Virgin LDPE with DMDAB melt blended samples (LDPE) before and after UV exposure, with dimensions 150 x 0.060mm were subjected to tensile tests as per ASTM D 638, using Universal Testing Machine (UTM) Lloyd Instrument Ltd UK. A cross head speed of 500mm/min and gauge length of 50 mm in both machine and transverse directions. The test under taken in an air conditioned at 20 °c.

3.4 Yellowness Test

Yellowness index of LDPE melt blended with DMDAB samples before and after UV exposure were calculated according to ASTM D 1925, by using BYK spectrophotometer.

3.5 Optical Properties

Optical properties such as luminous transmittance and haze were studied for the DMDAB blended samples (LDPE) before UV exposure and after UV exposure to find the effect of additive on the optical characteristics of the film. For measuring haze and luminous transmittance, The BYK Gardner Spectrophotometer was employed (ASTM D 1003).

3.6 Thermal Properties

3.6.1 Differential Scanning Calorimeter (DSC) Analysis

Melting behaviour of DMDAB blended samples (LDPE) are being studied by employing Perkin Elmer (USA) Differential Scanning Calorimeter under nitrogen atmosphere. Sample 5 mg weight were scanned from 45 to 200°C at the heating rate of 10°C/min to detect the melting characteristics of the sample before and after exposure to UV radiation. The percentage of crystallinity of DMDAB blended LDPE films were calculated as follows:

$$\% \text{crystallinity} = \frac{\Delta H_{f(\text{observed})}}{\Delta H_{f(100\% \text{crystalline})}} \times 100$$

Where ΔH_f is the enthalpy of the material and ΔH_f (100% crystalline) is the enthalpy of 100% crystalline material taken (277.3 J/g)

3.6.2 Thermo gravimetric analysis (TGA)

Thermal degradation of LDPE- DMDAB blended samples of before and after UV Exposure were analysed by Perkin Elmer (USA), at the heating rate of 10°C/min from 50 to 700°C in nitrogen atmosphere.

3.7 Fourier Transforms Infrared Spectroscopy (FTIR)

A Fourier Transform Infrared Spectrophotometer (FTIR) is also used to analyse the photo and bio degradable product and to analyse the rate of photo oxidation of the UV degraded films. The FTIR measurements used was a Perkin Elmer system 2000 infrared spectrum analyser with the wave number range of 400-4000 cm^{-1}

3.8 Biodegradation Test

DMDAB blended LDPE film was subjected to biodegradation test as per ASTM D 5338-98. The samples were exposed to inoculums that are derived from compost from municipal solid waste .The percentage of biodegradability is obtained by determining the percentage of carbon in the test sample that is converted into CO_2 during the duration of the test.

4. PERFORMANCE EVALUATION OF LDPE-DMDAB FILM

4.1 Mechanical Properties Evaluation

Exposed samples were subsequently tested for tensile strength measurement as per ASTM-D 638. Corresponding tensile strength values of the films is depicted in Table 3.

Table 3. Tensile strength of the LDPE-DMDAB film before and after UV exposure

| S. No | Sample Identification | Time | Transverse Direction (TD) /Machine Direction (MD) | Tensile Strength MPa | Young's Modulus MPa | % Elongation At Break |
|-------|-----------------------|-------|---------------------------------------------------|----------------------|---------------------|-----------------------|
| 1. | LDPE Virgin | - | MD | 11.27±0.42 | 90±0.52 | 324±0.23 |
| 2. | LDPE Virgin | - | TD | 10.25±0.32 | 115±0.34 | 453±0.34 |
| 3. | LDPE-DMDAB-1 | Day-0 | MD | 14.4±0.50 | 100±0.56 | 290±0.31 |
| 4. | LDPE-DMDAB-1 | Day-0 | TD | 13.04±0.46 | 155±0.53 | 503±0.41 |
| 5. | LDPE-DMDAB-1 | Day-1 | MD | 8.24±0.23 | 89±0.46 | 117±0.32 |
| 6. | LDPE-DMDAB-1 | Day-1 | TD | 7.94±0.21 | 94±0.48 | 52±0.36 |
| 7. | LDPE-DMDAB-1 | Day-2 | MD | 9.58±0.26 | 123±0.42 | 59±0.38 |
| 8. | LDPE-DMDAB-1 | Day-2 | TD | 9.02±0.25 | 118±0.49 | 38±0.30 |
| 9. | LDPE-DMDAB-1 | Day-4 | MD | 8.08±0.21 | 109±0.35 | 16±0.32 |
| 10. | LDPE-DMDAB-1 | Day 4 | TD | 6.49±0.29 | 112±0.39 | 8±0.29 |
| 11. | LDPE-DMDAB-3 | Day-0 | MD | 12.04±0.32 | 142±0.33 | 459±0.56 |
| 12. | LDPE-DMDAB-3 | Day-0 | TD | 9.53±0.35 | 143±0.38 | 335±0.52 |
| 13. | LDPE-DMDAB-3 | Day-1 | MD | 9.44±0.32 | 97±0.45 | 273±0.46 |
| 14. | LDPE-DMDAB-3 | Day-1 | TD | 9.23±0.43 | 110±0.41 | 159±0.34 |
| 15. | LDPE-DMDAB-3 | Day-2 | MD | 9.38±0.42 | 75±0.49 | 270±0.24 |
| 16. | LDPE-DMDAB-3 | Day-2 | TD | 7.87±0.20 | 124±0.43 | 112±0.43 |
| 17. | LDPE-DMDAB-3 | Day-4 | MD | 7.88±0.21 | 76±0.44 | 73±0.48 |
| 18. | LDPE-DMDAB-3 | Day-4 | TD | 6.39±0.26 | 104±0.39 | 65±0.51 |
| 19. | LDPE-DMDAB-5 | Day-0 | MD | 12.48±0.31 | 144±0.33 | 490±0.48 |
| 20. | LDPE-DMDAB-5 | Day-0 | TD | 11.10±0.22 | 155±0.38 | 467±0.44 |
| 21. | LDPE-DMDAB-5 | Day-1 | MD | 11.9±0.27 | 98±0.32 | 269±0.32 |
| 22. | LDPE-DMDAB-5 | Day-1 | TD | 10.51±0.32 | 96±0.41 | 286±0.39 |
| 23. | LDPE-DMDAB-5 | Day-2 | MD | 10.0±0.38 | 79±0.42 | 109±0.32 |
| 24. | LDPE-DMDAB-5 | Day-2 | TD | 9.82±0.35 | 78±0.44 | 55±0.35 |
| 25. | LDPE-DMDAB-5 | Day-4 | MD | 9.4±0.38 | 75±0.51 | 25±0.31 |
| 26. | LDPE-DMDAB-5 | Day-4 | TD | 8.02±0.41 | 75±0.53 | 12±0.23 |

MD- Machine Direction, TD- Transverse Direction, Day-0 – Without UV exposure, ± represents standard deviation.

It is evident that tensile strength of LDPE virgin increases with the incorporation of DMDAB to the tune of 1-3%. However on exposure of the blended samples to various cycles, there was a considerable decrease in the tensile strength of the samples. In case of the test sample containing 3% DMDAB, the deterioration in properties was observed from 12.04 MPa to 7.88 MPa (i.e. 34% degradation) within 4 days. For 1% DMDAB containing film the rate of degradation was 77%, which is highest in comparison to 3 and 5% DMDAB containing film.

Percentage of elongation at break and young's modulus is also decreased for samples when exposed to UV light. The LDPE-DMDAB 1% sample shows deterioration from 503% to 8% in

elongation at break (transverse direction) within 4 days, which is higher than 3 and 5% DMDAB containing film.

It was observed that with the increase of DMDAB content, the rate of photo degradation decreased, which is probably due to higher content of DMDAB, saturate the degradation at the time of photo degradation. The reason could be due to same UV region, DMDAB might have migrated during exposure and will not result in higher photo degradation of LDPE film and DMDAB bind with the matrix of LDPE, by virtue of its cohesive and adhesive force.

4.2 Yellowing Discoloration Evaluation

The polymer containing DMDAB increases its yellowness on exposure as shown in Table 4. Yellowness is defined as “the attribute by which an object colour is judged to depart from a preferred white towards yellow”. The Yellowness Index is a number calculated from spectral data that describes the change in colour of a test sample from clear or white toward yellow. This test is most commonly used to evaluate colour changes in a material caused by real or simulated outdoor exposure.

The yellowness index is calculated by using (ASTM D 1925):

$$YI = (100 \times 1.28X - 1.06Z) / Y$$

X, Y and Z are the tri-stimulus values for the calculated for illuminant C.

In polymer film causes low molecular weight species. The positive values of YI indicate increased yellowness and negative values indicates decreased yellowness. LDPE blended with DMDAB additives turns blue and the color of blueness increased with the percentage of additive. The LDPE- DMDAB 1, 3, 5% films shows higher yellowness index after exposure, which further confirms that UV wavelength above 300nm results in yellowing of virgin LDPE in presence of the additive. The rate of yellowness was highest in 3% DMDAB containing film.

Table 4. Yellowness Index of samples before and after UV exposure

| S No. | Sample Identification | Yellowness Index (YI) % |
|-------|-----------------------|-------------------------|
| 1. | LDPE-DMDAB-1 Day-0 | -9.16 |
| 2. | LDPE-DMDAB-1 Day -1 | 2.90 |
| 3. | LDPE-DMDAB-1 Day -2 | -2.36 |
| 4. | LDPE-DMDAB-1 Day -4 | -13.80 |
| 5. | LDPE-DMDAB-3 Day -0 | -2.85 |
| 6. | LDPE-DMDAB-3 Day -1 | 57.28 |
| 7. | LDPE-DMDAB-3 Day -2 | 45.65 |
| 8. | LDPE-DMDAB-3 Day -4 | -10.94 |
| 9. | LDPE-DMDAB-5 Day -0 | -2.57 |

When LDPE irradiated above 300 nm wavelengths in presence of air, oxidative degradation reaction may occur that results in the formation of other yellow products within a day of exposure for 1 and 3% containing DMDAB film. On further exposure the film turned transparent and became brittle after 4 days of exposure. This behavior probably was due to migration of additives at higher concentration of DMDAB. This may be the reason for 5% containing DMDAB film was not showing the degradation in comparison to 1 and 3 %

DMDAB film because the higher percentage of additives showing migration from the LDPE and the energy required for the photo degradation during UV exposure was used to migrate the DMDAB additive.

4.3 Optical Properties Evaluation

LDPE is widely used for packaging purpose and also undergoes UV exposure. The degradation mechanism can be understood by taking into account of light induced yellowing due to additive. The optical properties of LDPE with DMDAB & LDPE virgin are shown in Table 5.

Table 5. Optical properties of samples before UV exposure

| S. No | Sample Identification | Luminous Transmittance % | Haze % | Gloss |
|-------|-----------------------|--------------------------|--------|-------|
| 1. | LDPE Virgin | 89.93 | 21.38 | 10.6 |
| 2. | LDPE-DMDAB-1 Day-0 | 86.43 | 42.59 | 6.85 |
| 3. | LDPE-DMDAB-3 Day-0 | 83.60 | 74.62 | 2.9 |
| 4. | LDPE-DMDAB-5 Day-0 | 80.90 | 84.49 | 1.64 |

It is evident that with the increase in DMDAB concentration there was a decrease in transmittance level, which is probably due to the presence of photo-oxidative degradation species. In case of the film containing 1% DMDAB the optical properties deteriorated significantly because of faster rate of degradation in these samples. These results are in agreement with the mechanical properties thus revealing higher degradation rate at lower additive percentage.

4.4 Thermal Properties

The kinetics of thermal degradation was measured employing DSC & TGA.

4.4.1 Differential Scanning Calorimeter (DSC)

The virgin LDPE shows its melting point at 114°C. On the incorporation of 1% DMDAB, the melting point is increased by 3°C i.e. 117.37°C due to the presence of additive in LDPE matrix as shown in Figures 3 and 4. Exposure of the samples in UV radiation, showed a clear trend of degradation. In case of the samples exposed for 1 day, a marginal decrease in the melting point of LDPE from 117 to 110.8°C was observed. Corresponding ΔH value also decreased drastically indicating formation of low molecular weight species. A similar decrease in the percentage of crystallinity was also noticed. The percentage of crystallinity and melting point is given in Table 6.

Table 6. Results of DSC melting point, enthalpy and degree of crystallization for LDPE –DMDAB samples

| S. No | Sample Identification | Peak Value °C | Enthalpy (H) J/G | Degree of Crystallinity X_c |
|-------|-----------------------|---------------|------------------|-------------------------------|
| 1. | LDPE Virgin | 114.93 | 132.069 | 100 |
| 2. | LDPE-DMDAB-1 Day-0 | 117.37 | 79.735 | 60.37 |
| 3. | LDPE-DMDAB-1 Day-1 | 110.48 | 43.045 | 32.59 |
| 4. | LDPE-DMDAB-1 Day-2 | 110.53 | 56.535 | 42.80 |
| 5. | LDPE-DMDAB-1 Day-4 | 110.88 | 81.829 | 61.96 |
| 6. | LDPE-DMDAB-3 Day-0 | 112.68 | 42.863 | 32.46 |
| 7. | LDPE-DMDAB-3 Day-1 | 111.19 | 50.468 | 38.21 |
| 8. | LDPE-DMDAB-3 Day-2 | 110.88 | 50.990 | 38.61 |
| 9. | LDPE-DMDAB-3 Day-4 | 109.88 | 40.874 | 30.95 |
| 10. | LDPE-DMDAB-5 Day-0 | 113.03 | 67.934 | 51.43 |

On further exposure, the values are more or less constant showing that the maximum - degradation has occurred in one-day exposure. For LDPE-DMDAB the melting point has come down from 114 to 112°C showing a marginal incompatibility of additive with LDPE. This further indicates that polymer starts degrading and deterioration in other properties also provides additional evidence in degradation phenomenon.

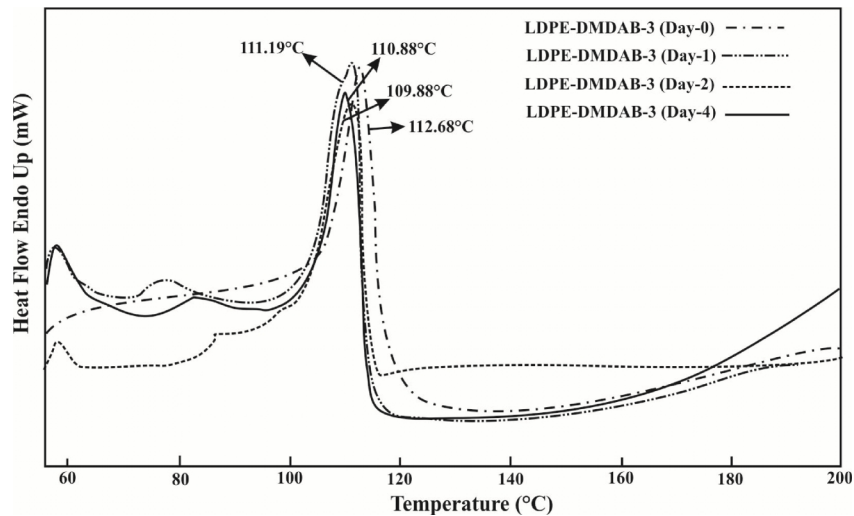


Figure 3. Plot of DSC curves for 1% LDPE-DMDAB before and after exposure to UV radiation

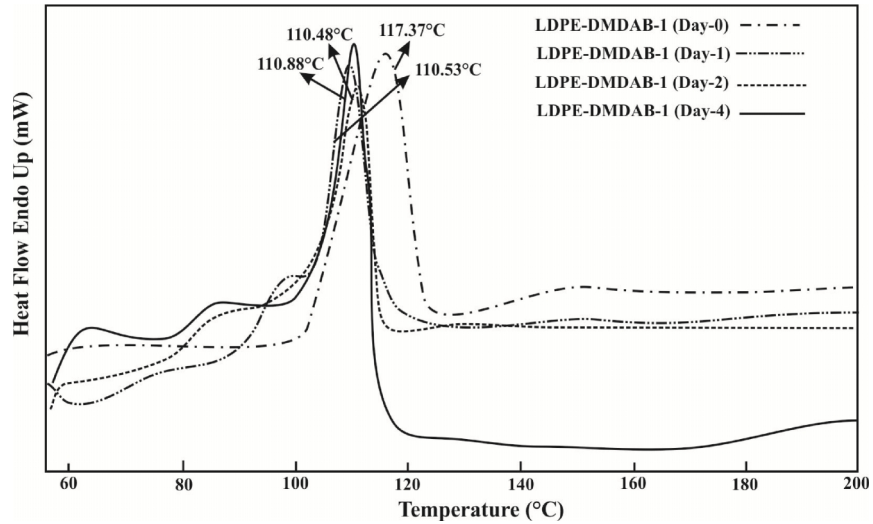


Figure 4. Plot of DSC curves for LDPE-3% DMDAB before and after exposure to UV radiation

4.4.2 Thermo gravimetric Analysis (TGA)

The kinetics of thermal degradation was observed for film containing photodegradable additive at 1, 3 & 5% and their TGA curve is shown in Figure 5. The TGA thermo grams after UV exposure for LDPE-1% DMDAB, LDPE-3% DMDAB and LDPE-5% DMDAB are shown in Figures 6, 7 and 8 respectively. The data derived from thermal degradation is given in Table 7.

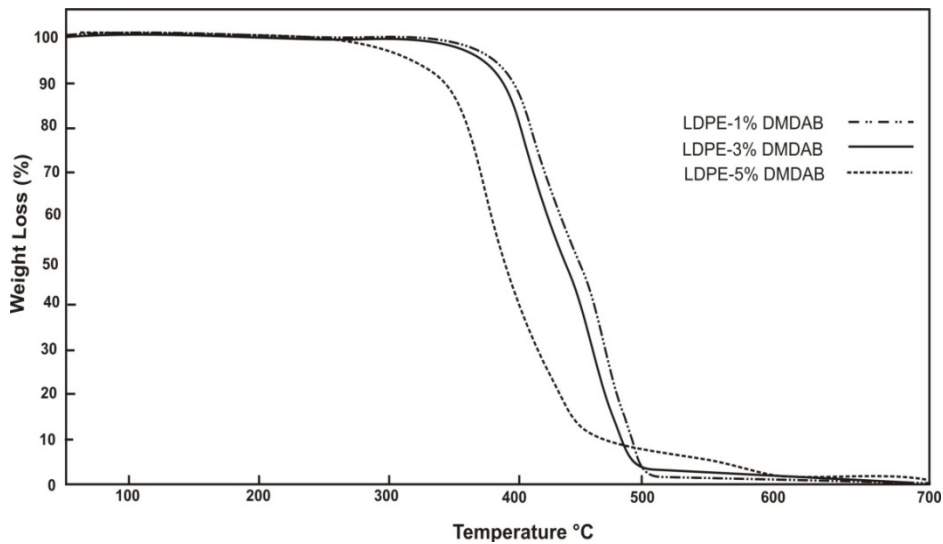


Figure 5. TGA thermo gram for LDPE-DMDAB 1, 3 and 5 before exposure to UV radiation

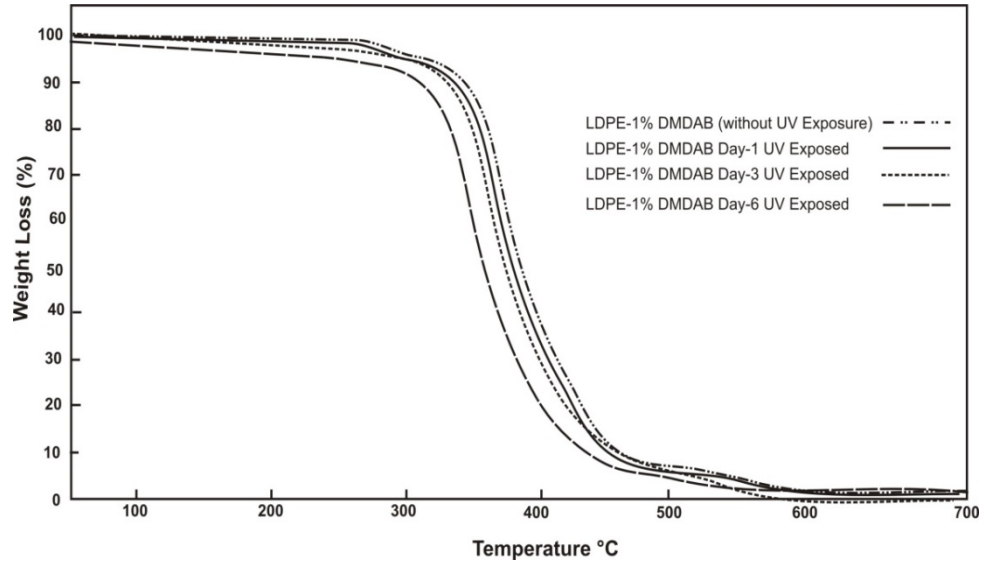


Figure 6. TGA thermo gram for LDPE-1% DMDAB after exposure to UV radiation

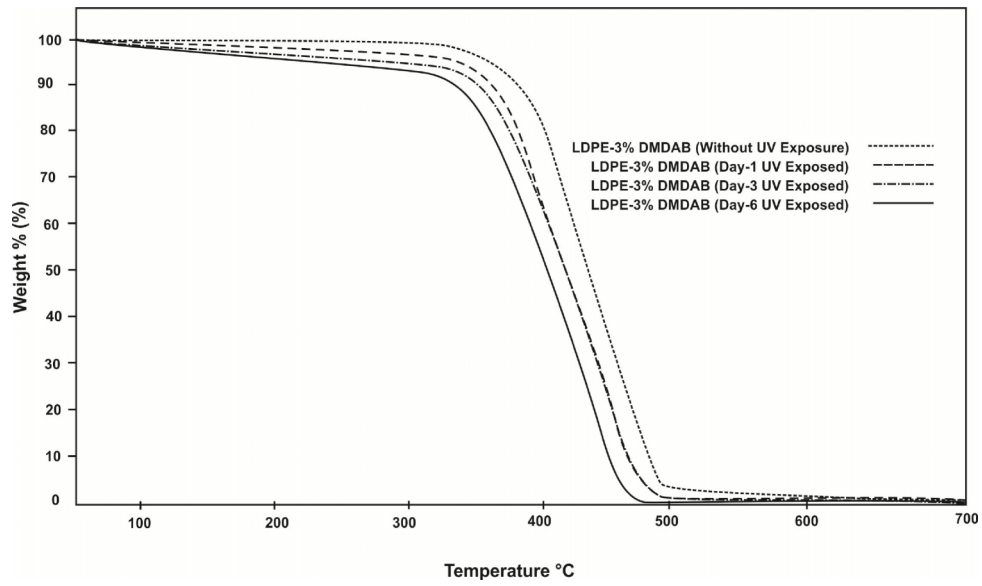


Figure 7. TGA thermo gram for LDPE-3% DMDAB after exposure to UV radiation

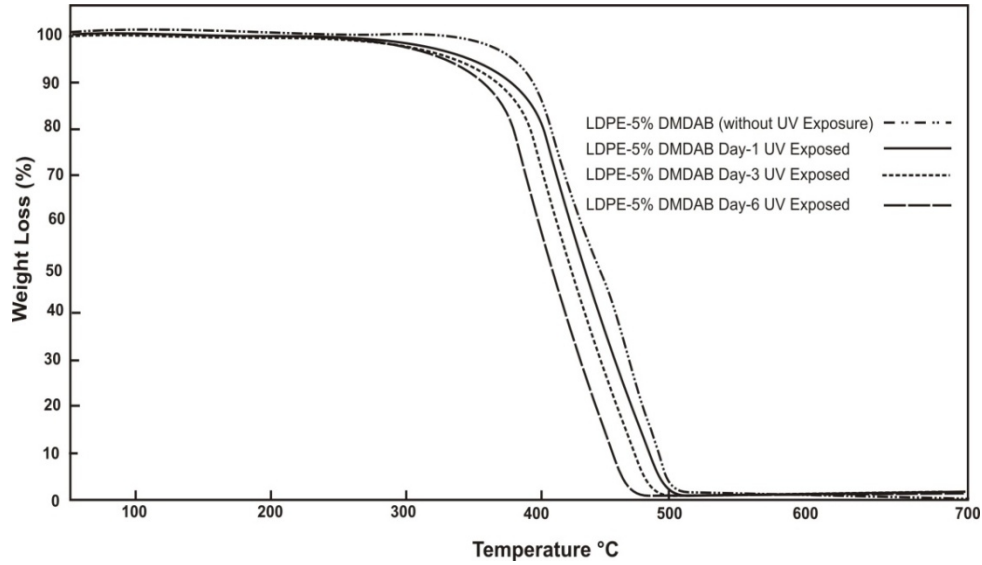


Figure 8. TGA thermo gram for LDPE-5% DMDAB after exposure to UV radiation

Table 7. Results of TGA Characterization for samples after exposure

| S. No. | Designation of Matrix | IDT (°C) | D _{1/2} T (°C) | UDT (°C) |
|--------|-----------------------|----------|-------------------------|----------|
| 1. | LDPE Virgin | 392 | 460 | 510 |
| 2. | LDPE- DMDAB-1 Day-0 | 388 | 451 | 504 |
| 3. | LDPE- DMDAB-2 Day-0 | 383 | 441 | 490 |
| 4. | LDPE- DMDAB-3 Day-0 | 351 | 388 | 448 |
| 5. | LDPE- DMDAB-1 Day-1 | 349 | 384 | 445 |
| 6. | LDPE- DMDAB-1 Day-3 | 340 | 378 | 430 |
| 7. | LDPE- DMDAB-1 Day-6 | 325 | 363 | 415 |
| 8. | LDPE- DMDAB-3 Day-1 | 357 | 416 | 472 |
| 9. | LDPE- DMDAB-3 Day-3 | 361 | 422 | 475 |
| 10. | LDPE- DMDAB-3 Day-6 | 352 | 412 | 463 |
| 11. | LDPE- DMDAB-5 Day-1 | 385 | 443 | 497 |
| 12. | LDPE- DMDAB-5 Day-3 | 384 | 433 | 483 |
| 13. | LDPE- DMDAB-5 Day-6 | 376 | 412 | 466 |

From the Figure 5, the sample containing 5% DMDAB shows higher thermal stability as compared to 1% and 3% DMDAB film before subjected to UV exposure. The thermal stability of the samples after 1 day UV exposure for 1% DMDAB the Initial Decomposition Temperature (IDT) decreased from 388°C to 349°C and after 6 days exposure decreased 325°C. The 17% deterioration was observed for the 1% DMDAB film. The thermal degradation was highest in the case of 1% DMDAB containing film and the other samples containing 3 and 5 % DMDAB also showing linear degradation on UV exposure from day 1 to day 5. The data presented in Table 7 clearly indicates that the effects of thermal stability (Initial Decomposition Temperature, IDT, Decomposition at half, D_{1/2}T, and Ultimate Decomposition Temperature, UDT) are decreased on blending with the DMDAB. The thermal degradation of samples containing DMDAB leads to the production of low molecular weight volatile materials as well as low molecular weight compounds as indicated in the results. The

thermal stability of the 3% DMDAB is increased from 351 to 376°C after 6-days of UV exposure. The abnormality in the results of the thermal stability of 3% DMDAB sample could be due to the migration of the additives during UV exposure.

4.5 Fourier Transform Infrared Spectroscopy (FTIR)

The structural unit of DMDAB is shown in Figure 1. For comparison an infrared spectrum of LDPE & DMDAB is shown in Figure 9 and comparison of characteristic peak assignment values in FTIR spectra for virgin LDPE and DMDAB shown in Table 8. Polymer became yellow, tacky and opaque during UV exposure. Before UV exposure for the samples containing 1, 3 and 5% DMDAB film is shown in Figure 10 and after exposure FTIR is shown in Figures 11,12 and 13 for DMDAB containing LDPE film 1% 3 % and 5% respectively.

Table 8. Characteristic peak values in FTIR spectra for virgin LDPE and DMDAB

| S. No. | Absorption bands (cm^{-1}) and their peak assignments LDPE (Low density Polyethylene) | |
|------------------------------------------------|-----------------------------------------------------------------------------------------------------|-----------------------------------------------|
| 1. | 545 | -CH ₂ Rocking Vibration |
| 2. | 1464 | -CH ₃ anti symmetric deformation |
| 3. | 1472 | -CH ₂ symmetric deformation |
| 4. | 1377 | -CH ₃ symmetric deformation |
| 5. | 2937 | -CH ₂ anti symmetric deformation |
| 6. | 2896 | -CH ₃ symmetric stretching |
| 4,4, bis (dimethyl amino benzophenone) (DMDAB) | | |
| 7. | 1598 | C ₆ H ₅ -N-C stretching |
| 8. | 1715 | -C=O stretching |
| 9. | 742 | =C-H out of plane bend |
| 10. | 3087 | =C-H stretching |
| 11. | 1532 | -N-CH ₃ deformation |

For LDPE-DMDAB 1%, a new peak corresponding to 1598 cm^{-1} was observed. The appearance of C₆H₅-N-C stretching peak confirms the presence of additive in LDPE. On increase of percentage of DMDAB the peak at 1598 cm^{-1} increases showing the increase in percentage of additive in LDPE. One day exposure shows -C=O stretching indication due to formation of carbonyl compound on chain scission of LDPE. On increase of time of exposure from day 1 to day 4, there was an increase of intensity of 1715 cm^{-1} peak and disappearance of -N-H stretching peak i.e. 1598 cm^{-1} . This was the evidence of degradation products that probably consist of carbonyl and oxygen containing compound.

In further exposure to UV, there is an increase of chain scissoring and formation of low molecular weight compound. Carbonyl region group is enriched due to degradation product at 1463 cm^{-1} . On UV exposure, there was clear indication of formation of low molecular weight product with 3% DMDAB film and formation of carbonyl containing compound i.e. 1715 cm^{-1} showing after two days exposure. The intensity of 1598 cm^{-1} remained for two days indicating the presence of additive in the film. The degradation structure could not be fully detected from the results shown here but the retention of 1715 -C=O cm^{-1} stretching peak suggested the formation of low molecular weight product after chain scissoring of LDPE.

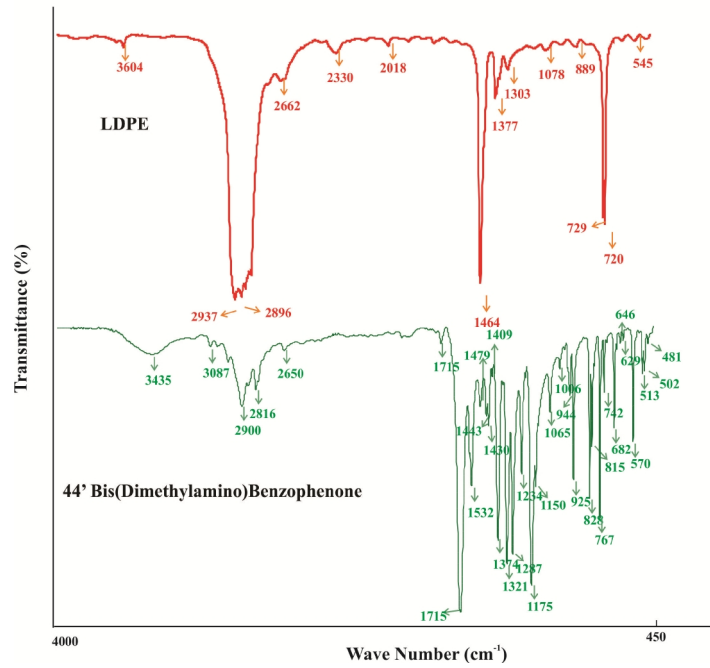


Figure 9. FTIR spectra of Virgin LDPE and DMDAB

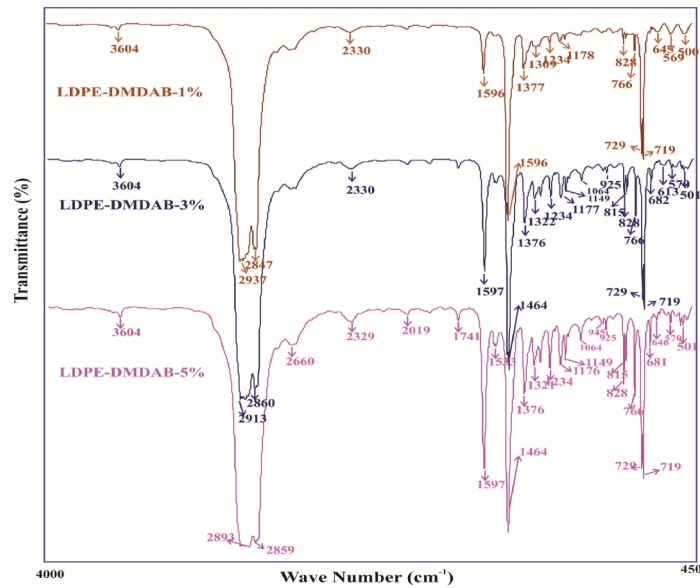


Figure 10. FTIR spectra for LDPE-1, 3 and 5% DMDAB before exposure

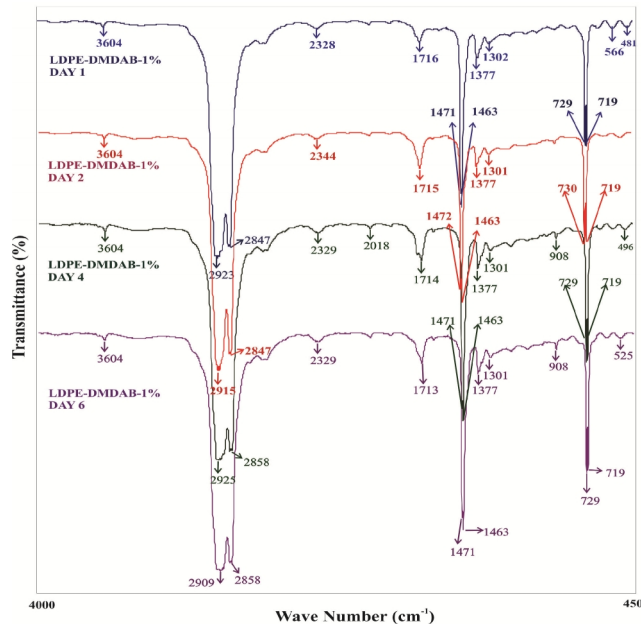


Figure 11. FTIR spectra for LDPE-DMDAB-1% after exposure

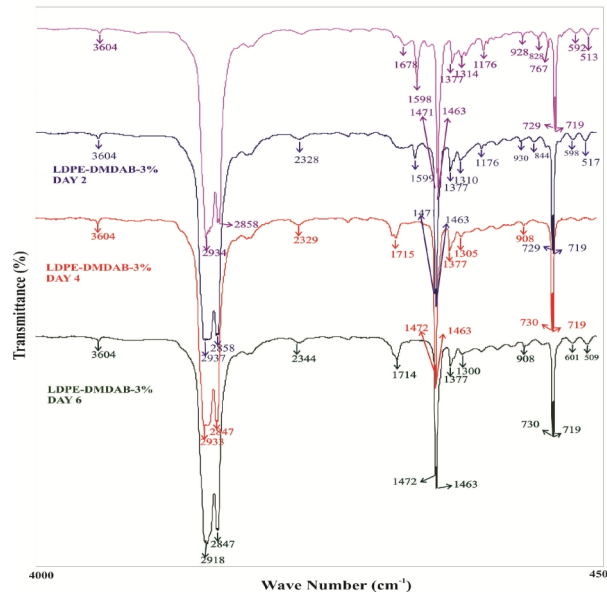


Figure 12. FTIR spectra for LDPE-DMDAB-3% after exposure to UV radiation

The morphology of the LDPE-DMDAB blended film was studied using a scanning electron microscope (JEOL JSM 840A, Japan) with the samples surface was coated with gold of 10 A° for examination of morphology with an accelerating of 20kV. The morphology after blending and after UV exposure of the samples has been taken for 1, 3 and 5% containing DMDAB film and given in Figure 14.

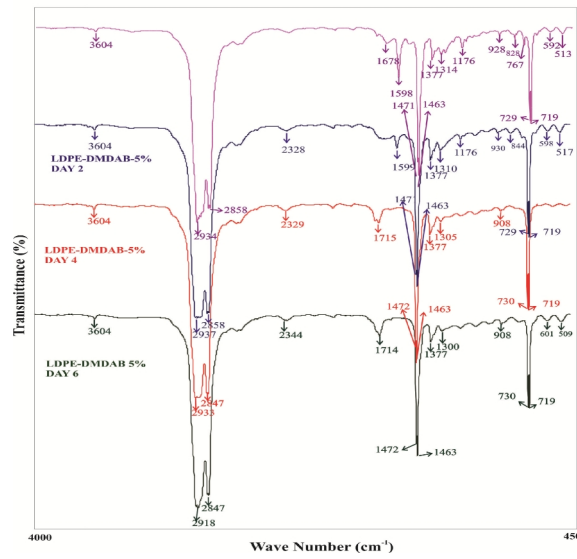


Figure 13. FTIR spectra for LDPE-DMDAB-5% after exposure to UV radiation 4.6 Scanning Electron Micrograph (SEM)

The LDPE-DMDAB blended film with 1, 3 and 5% of additives showing good dispersion on the blending and the uniform dispersion can be seen from the micrograph given below:

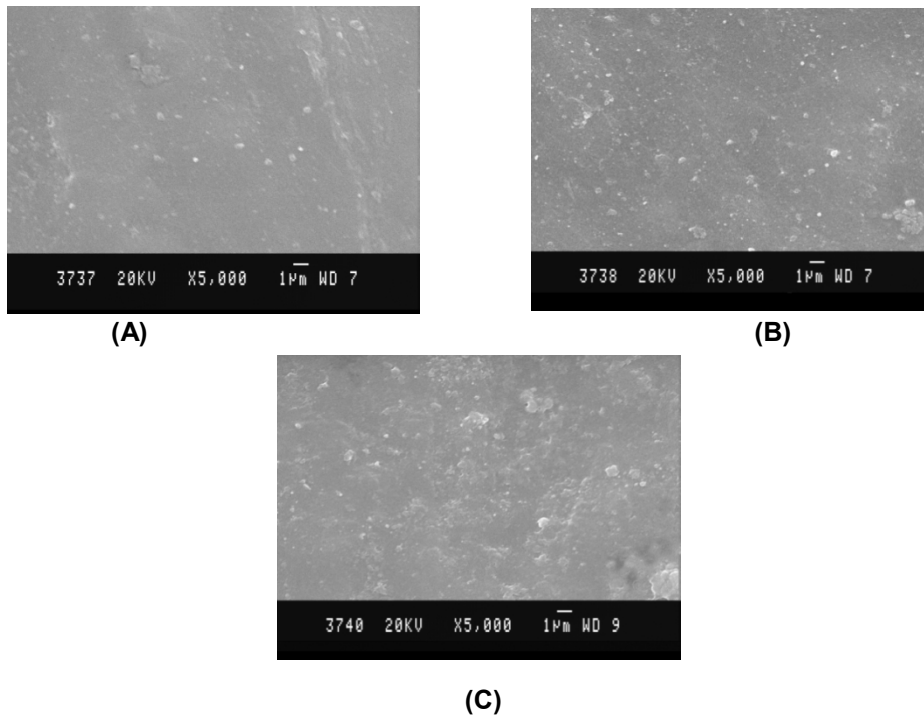


Figure 14. (A) LDPE-DMDAB-1% Before UV exposure (B) LDPE-DMDAB-3% Before UV exposure (C) LDPE-DMDAB-5% Before UV exposure

On UV exposure the degraded samples was again subjected to SEM analysis to study the surface analysis of the samples and the same has been given in Figure 15. From the Figure given below can be seen that on UV exposure the degradation of the chain scissoring takes place and the polymer samples are in brittle stage. This can be visualized that the sample containing 1% DMDAB degraded more.

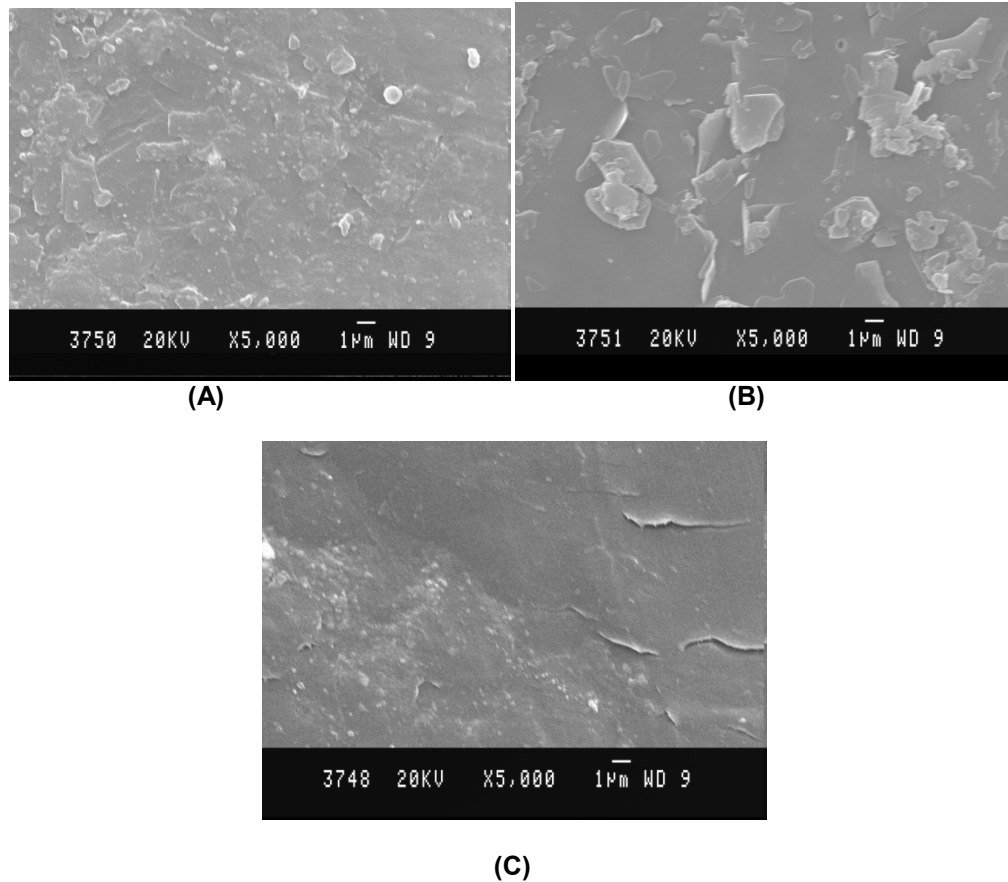


Figure 15. (A) LDPE-DMDAB-1% After UV exposure (B) LDPE-DMDAB-3% After UV exposure (C) LDPE-DMDAB-5% After UV exposure

4.7 Subsequent Bio-degradation of the Photodegradable Film

Biodegradation testing in the laboratory-scale compost was conducted according ASTM 5338-98. A series of twelve composting vessel (three test specimen, blank, negative and positive control) were repeatedly tested twice time. Mixture of testing organic fraction solid compost (600 g dry basis) and test specimen (10g on dry basis) were introduced and incubated at $58\pm 2^{\circ}\text{C}$. The air flow rate controlled between 15 ml/min. The CO_2 evolved was absorbed by 0.024 N $\text{Ba}(\text{OH})_2$ and the amount of CO_2 was determined by titrated the solution with 0.05 N HCl (frequency every or the first 2 to 3 week and after every 1 to 3 week).

The sample of LDPE film modified with DMDAB additives were oxidized by oven ageing, and the fragments incubated with cultures of a bacterium *aspergillums niger* and *pencilium funiculosum*.

Calculation

1. The total carbon content (Ci) in the test material was determined by elemental analysis.
2. Cumulative CO₂ produced in grams (Cg test) from the test sample, was calculated.
3. Cumulative CO₂ produced in grams (Cg blank) from the blank (compost) sample was calculated.
4. Percentage of biodegradation was determined by dividing the net average gaseous carbon produced in the test compound by the original average amount of carbon in the test compound and multiplying it by 100.

$$\frac{Mean C_g (test) - Mean C_g (blank)}{C_i} \times 100$$

Where, C_g = amount of gaseous carbon produced, gm,

C_i = amount of carbon in test compound added, gm

4.7.1 Observation for biodegradability test as per ASTM D-5338

1. Sample detail: Light Yellow Color photo-degraded Film

2. Observation

(1) Conditions of reaction mixtures

Origin of compost: Live stock excrement, municipal and vegetable waste
 Reaction Temperature : 58⁰C (± 2⁰C)
 Dry Solid (%) : 52
 Volatile Solid (%) : 19
 Air flow rate : 100 ml/min
 Test duration (day) : 50 days
 Reference material : Cellulose
 Volume of reaction vessel : 3000 ml
 Moisture percentage in compost : 27 %

(2) pH of test medium (before and after an examination):

| Composting Vessel (Material with test medium) | | p ^H (before) | p ^H (after) |
|-----------------------------------------------|--------------------------|--------------------------|-------------------------|
| 1 | Sample 1(LDPE-DMDAB- 1%) | 7.6 | 7.9 |
| 2 | Sample 2(LDPE-DMDAB-1%) | 7.6 | 7.8 |
| 4 | BLANK | 7.6 | 7.7 |
| 5 | Positive (cellulose) | 7.6 | 8.1 |
| 6 | Negative (PE film) | 7.6 | 7.8 |

Sample 1: 16.29 %; Sample 2: 14.69 %; MEAN: 15.49 %
 The reference material cellulose 100.0 %

Sample 1 and sample 2 are the same sample and the mean results reported for LDPE and 1% DMDAB sample.

3. Results

The curve of biodegradation is shown in Figure 16. and Percentage biodegradation relative to positive reference.

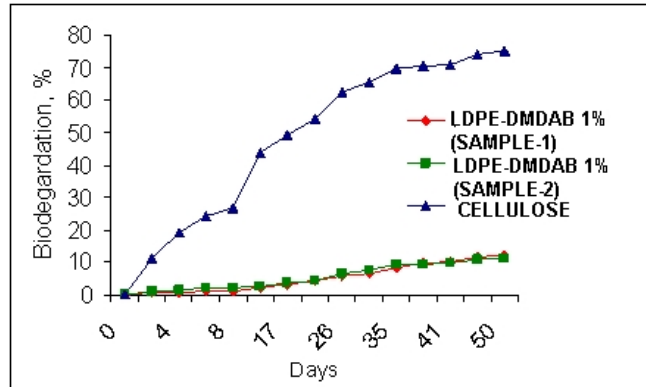


Figure 16. Bio-degradation curve for the photodegradable product of LDPE 1% DMDAB film

The LDPE-DMDAB was initially subjected to photo degradation and subsequent biodegradation using compost method was showing quit sufficient amount of biodegradation i.e. ~16% (percentage of biodegradation) within 50 days. The correlation can be done from the above studies that an increase in the number of days could increase in the percentage of biodegradation. This shows that the photodegradable product will lead to the biodegradation and this can be increased if the photo degradation will be higher at the initial stage. The reason for the biodegradation could be the formed low molecular weight product will lead to fragment easily by enzymatic action during biodegradation.

5. CONCLUSION

The performance evaluation of photo and biodegradation of LDPE-DMDAB blended films are concluded as:

1. The mechanical property showed deterioration within one day of UV irradiation for 1% additive containing film. There was a drastic drop in the elongation of the sample after one day itself and the film was unusable for the mechanical test after day four. The film samples used were found to become brittle from the day four of exposure. The degradation in the mechanical properties for 1% DMDAB is much higher than that of 3 and 5% DMDAB containing film.
2. The yellowness index value increases in polymer after one-day exposure for all the samples. The 3% additives containing film is showing highest yellowness after one day. On further exposure the entire samples became transparent and brittle due to the migration of additives from film. The migration increases with increase of DMDAB

percentage. That could be the reason for highest degradation achieved in 1% DMDAB film and at 3% and 5% concentration the percentage of degradation is less as compared to 1% degradation. The higher concentration will lead to form incompatibility of the additives with the LDPE and it is migrating when exposed to UV radiations. It can be confirms that the 3% and 5% DMDAB containing polymer tend to decrease its yellowness index after one day of exposure showing migration of the additives after one day exposure.

3. The DSC result showed a decrease in the melting point and degree of crystallinity in the exposed samples of 1, 3 and 5% DMDAB containing samples. The degree of crystallinity was reduced by about 60% in one-day exposure for 1% additive containing film. This confirms the effect of DMDAB as a photodegradable additive.
4. The TGA also confirms the formation of low molecular weight substances because of degradation of LDPE film the thermal stability of the film decrease about 20% for the 1% DMDAB. The highest thermal degradation was found in 1% and the migration of the additives during exposure once again confirm for the 3% DMDAB because the thermal stability is increased for the sample.
5. The FTIR studies also showed that 1% additive has more degradation as compared to 3 and 5% containing film. On increase of time of exposure from day 1 to day 4, the spectrum was showing the evidence of degradation products that consist of carbonyl and oxygen containing low molecular weight compound.
6. The morphology results are showing there was a degradation product after photo degradation.
7. The subsequent biodegradation of the 1% DMDAB photodegradable film was showing only **16% biodegradation** after 50 days.

The results detailed in this work shows that DMDAB can be used, as an effective photodegradable additive. The photo degradation rate of the additive is very high at lower concentration of DMDAB additive and the biodegradation was also proving that some low molecular weight species was formed during photo degradation, which is responsible for the 16% biodegradation.

COMPETING INTERESTS

Authors have declared that no competing interests exists.

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