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Polymer Degradation and Stability 90 (2005) 577–585

Polymer Degradation and Stability

www.elsevier.com/locate/polydegstab

Effect of benzil and cobalt stearate on the aging of low-density polyethylene films

P.K. Roy[a], P. Surekha[a], C. Rajagopal[a], S.N. Chatterjee[b], V. Choudhary[c,]*

[a]*Centre for Fire, Explosive and Environment Safety, Brigadier. S. K. Majumdar Marg, Delhi 110054, India*
[b]*Solid State Physics Laboratory, Timarpur, Delhi 110054, India*
[c]*Centre for Polymer Science and Engineering, Indian Institute of Technology, Hauz Khas, Delhi 110016, India*

Received 26 November 2004; received in revised form 12 January 2005; accepted 18 January 2005

Abstract

We report an investigation of the effect of benzil and cobalt stearate on the degradation behaviour of LDPE films. Thin films (70 μ) containing these additives were prepared by sheeting process. The effect of heating, exposure to UV-B and natural weathering of LDPE films in the presence/absence of additives was investigated. Changes in the tensile properties, carbonyl index and density were used to investigate the degradation behaviour. Attempts have been made to correlate the results as a function of mixed additives. In contrast to the activity of typical triplet activators, benzil was found to be incapable of initiating thermal- or photo-degradation of LDPE films. However, an accelerated rate of oxidation was observed, primarily due to cobalt stearate, in the case of compositions containing a combination of benzil and cobalt stearate. All samples were found to be more susceptible to thermo-oxidation than to UV or natural weathering.

Keywords: LDPE; Benzil; Weathering; Photo-oxidation; Thermo-oxidation

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1. Introduction

Polyethylene has achieved a dominant position as a packaging material because of its relatively low cost, versatile properties including high tensile strength, elongation at break, good barrier properties against water borne organisms, lower cost, higher energy effectiveness, light weight and good water resistance. However, it has been a target of much criticism due to its lack of degradability [1]. Attempts to produce a low cost packaging material from polyolefins dates back to the second half of the 20th century [2]. Major strategies to facilitate polyethylene disintegration are focused on direct incorporation of carbonyl groups within the backbone or their in-situ generation by addition of pro-oxidant. Typical pro-degradants include UV activators like aromatic ketones, transition metal ions and their complexes.

In this work we have attempted to investigate the effect of benzil and cobalt stearate on the degradation behaviour of low-density polyethylene (LDPE) films. The polymer was chosen keeping in mind its prime importance in the packaging field and its inherent resistance towards degradation. Benzil, being an aromatic ketone is expected to give rise to long-lived triplet states on exposure to UV radiation. Aromatic ketones have been reported to act as effective photo-initiators for several polymers [3–8]. Addition of diphenylketone has also been reported to increase the photo-oxidative degradation of LDPE films containing cerium stearate [9]. However, the effect of benzil on the

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* Corresponding author. Tel.: +91 11 26591423; fax: +91 11 26591421.
E-mail address: veenach@hotmail.com (V. Choudhary).

0141-3910/$ - see front matter
doi:10.1016/j.polymdegradstab.2005.01.017

degradation behaviour of LDPE has not been studied systematically. Benzil, due to its two ketonic groups is expected to have a stronger degradative effect as compared to the analogous benzophenone having one keto group.

The effect of benzil has also been compared with that of cobalt stearate, which is a conventional metallic photo-initiator. The role of metallic photo-initiators in the degradation of polyethylene has been extensively studied by various authors [10–12]. However, the combined effect of benzil and cobalt stearate has not been investigated.

Natural, artificial weathering and thermo-oxidative weathering of LDPE films containing cobalt stearate, benzil and combination of both were performed and the physico-chemical changes were monitored by FTIR, tensile properties and apparent density measurements.

2. Experimental

2.1. Materials

Benzil, cobalt acetate, sodium hydroxide and stearic acid (AR grade E.Merck) were used without further purification. Commercial low-density polyethylene (LDPE) (Indothene, 24FS040) was used for the preparation of films. The MFI for the polymer was 4 g/10 min, with crystalline melting point of 110 °C and density of 0.92 g/cm^3. Cobalt stearate was prepared by double decomposition of cobalt acetate with sodium stearate according to a procedure reported in the literature [13].

2.2. Preparation of films

A Brabender plasticorder Labstation with a 19 mm diameter screw of L:D = 25:1, extruder speed of 20 L/min associated with a roller having a draw speed of 3 m/min was used for the preparation of films. LDPE chips were dry blended with varying amounts of benzil ranging from 0.1–0.5 % w/w in a tumbler and then fed to the Brabender. The temperatures in the feed zone, 150 °C; compression zone, 165 °C; metering zone, 175 °C and die zone 190 °C were used for extrusion. At concentrations higher than 0.5 % w/w of benzil, the compounds exhibited a blooming effect. LDPE films were also obtained by using mixture of benzil and cobalt stearate. In all the formulations the concentration of benzil was kept constant at 0.1 % w/w whereas the concentration of cobalt stearate was varied from 0.05 to 0.1 % w/w. The details of formulations and the sample designations are given in Table 1. Neat LDPE film has been designated as F1 and films having benzil and mixtures of benzil and cobalt stearate have been designated as FB and FBC followed by numerical suffix indicating the amount of cobalt stearate multiplied by 100. For example, LDPE films containing 0.1% benzil + 0.05% cobalt stearate and 0.1% benzil + 0.075% cobalt stearate have been designated as FBC-5 and FBC-7.5, respectively.

Table 1
Details of formulations and their sample designation

Sample designation	Amount		
	LDPE	Benzil	Cobalt stearate
F1	100	–	–
FB-1	100	0.1	–
FB-3	100	0.3	–
FB-5	100	0.5	–
FBC-5	100	0.1	0.05
FBC-7.5	100	0.1	0.075
FBC-10	100	0.1	0.1
FC-1	100	–	0.1

2.3. Degradation studies

2.3.1. Thermo-oxidative tests

The thermo-oxidative test was carried out by placing the extruded films in an air oven at 70 °C for extended periods as reported in the literature [12,14]. The changes due to thermo-oxidation were monitored using FTIR, tensile properties and density.

2.3.2. Natural weathering

Duplicate sets of films were exposed at the Centre of Fire, Explosive & Environment Safety facing the south direction with an inclination angle of 45°. The site is located at 28°63′N and 77°12′E. These experiments were started in the month of February 2004.

2.3.3. Photodegradation studies

Accelerated photodegradation studies were carried out using four 40 W sunlamps emitting light in the wavelength range of 280–350 nm with maxima at 313 nm. Samples were mounted on racks positioned at a distance of 5 cm from the lamps and the temperature in the cabinet was maintained at 30 ± 1 °C. Samples were collected at regular intervals to evaluate the effect of irradiation time on degradation.

2.4. Evaluation of degradation

Changes in the mechanical properties, i.e. tensile strength and elongation at break, were monitored using a Materials testing machine Model JRI-TT25. Samples with a gauge length of 100 mm and width of 10 mm were cut from the films for tensile strength measurements as per ASTM 882-85. The speed of testing was 100 mm/min. The tests were undertaken in an air-conditioned environment at 20 °C and a relative humidity of 65%. About five samples were tested for each experiment and the average value was taken.