

The Effect of Cobalt Naphthenate and 2-benzoylbenzoic Acid on UV-Degradation of LDPE

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Abstract

The effect of cobalt naphthenate and 2-benzoylbenzoic acid on UV-photooxidative degradation of low density polyethylene have been studied. Sheets of these samples were prepared from polyethylene and different concentrations of cobalt naphthenate and 2-benzoylbenzoic acid then these samples were UV-irradiated. Changes in the carbonyl index, tensile strength, elongation at break, crystallinity and density were measured to monitor the degradation. The measurements were done before and after UV-irradiation at every 30-day interval for 90 days. The results show that the UV-irradiation affects the rate of degradation of LDPE with increasing the concentration of the cobalt naphthenate and 2-benzoylbenzoic acid. The increasing rate of degradation is more obvious for the increased concentration of cobalt naphthenate and also the time of irradiation, but the rate of degradation is decreased by incorporation of 2-benzoylbenzoic acid.

Keywords: *Mechanical Properties, Photooxidative Degradation, UV-degradation, Cobalt Naphthenate, 2-benzoylbenzoic Acid*

1- Introduction

Polyethylene has had good properties such as high tensile strength, elongation at break, good barrier properties against water born organisms, good water resistance, light weight and relatively low cost to increase its demand in recent years. The increase in demand for polymer material, especially in packaging industries, is responsible for the generation of polymer waste, so the attention for degradable polymers was developed [1].

Many studies have been done for investigating photodegradation of low density polyethylene and its copolymers. Many of these studies were carried out by irradiating the material, in the presence or absence of oxygen, with UV radiation having wavelengths near to those of the UV component of sun light. [2-6]

Cruz-Pinto et al [7] studied the kinetics and mechanism of the natural and accelerated photo-oxidation of low density polyethylene (LDPE) films by developing kinetic models

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of the photo-oxidation process to interpret and predict the results of measurements of carbonyl, hydroperoxide and vinyl absorbance as functions of time and temperature. The models predict the general experimental behavior, and also the formation of both hydroperoxides and carbonyl. Norrish-I reactions are important initiation steps.

Irradiation of polyethylene at elevated temperatures can lead to further deterioration of combined thermal and Photo-oxidation. [8]. The physical and chemical changes occurring involve the increase in concentration of a variety of oxygen-containing groups in addition to the promotion of cross linking and chain scission. The oxygen-containing groups include hydroperoxide, peroxide, and various carbonyl-containing moieties, in particular the ketonic carbonyl. These initiate further photo-oxidation in the polymer by undergoing reaction of the Norrish I and II types typically observed during the oxidation of hydrocarbons.

The initiation of photodegradation is due to chromophores acting as photochemical impurities in the polymers, and capable of absorbing the radiation energy. The excited states are formed and undergo photo-chemical reactions [9].

Polyethylene is one of the most widely studied polymers, particularly concerning its degradation under environmental conditions. A study has also been made on the influence of processing conditions on the degradation of low density polyethylene [10]

The structural changes in Low Density Polyethylene (LDPE) were studied by photoageing samples of the material with

different supermolecular structures. It was found that the primary molecular structure of polyethylene significantly affects both physical and chemical changes which take place in LDPE during photoageing [11, 12]. The carbonyl profiles of naturally and artificially weathered low density polyethylene samples have been studied and it was found that to exhibit the same characteristics just below the exposed surface, the carbonyl concentration falls to a level which remains reasonably constant to a depth of about 0.8 mm [13].

Environmental degradation of stabilized low density polyethylene films up to 12480 h. of exposure were studied [14, 15]. It was found that the highest concentration of carbonyl and vinyl groups is between 8000-10500 h. of exposure time. It was also concluded that a stabilized low density polyethylene film exposed outdoors undergoes the processes of photo-oxidation and degradation, which results in a large reduction in its physical-mechanical characteristics and in the thermal oxidation strength.

The action of anthraquinone sensitizers on the photooxidative degradation of low density polyethylene was studied by using films of the polymer containing three quinoid sensitizers and these films had been exposed to light. The kinetics of the photo-oxidative degradation had been monitored by the IR-spectra and mechanical properties [16].

Geetha et al [17] studied the effect of polymer characteristics on chemical changes and mechanical properties on the photo-oxidative degradation of polyethylene.

The effects of benzophenone (BP) on the photodegradation of polyethylene were investigated by analyzing the ESR and

infrared spectra of the irradiated samples [18].

Albertsson et al [19] aged low density polyethylene samples in a weatherometer and analyzed these samples by FT-IR and differential scanning calorimetry to monitor the changes in the carbonyl index and crystallinity during photo-oxidation. Volatile low molecular weight degradation products were detected using head-space gas chromatography and changes in tensile strength were monitored.

Representative samples of commercial photodegradable polyethylene were examined with respect to the rate and extent of oxidation by measuring the carbonyl (carboxylic acid and ester) formation, molar mass reduction and ability to support microbial growth when used as the only source of carbon [20].

The in-depth of unprotected low density polyethylene (LDPE) induced by photo-oxidation had been studied by following the carbonyl content and other by-product groups as well as the retention of mechanical properties as a function of time and distance from the surface [21].

2-benzoyl benzoic acid, 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 photoinitiators for several polymers [22]. In our previous studies we reported the effect of cobalt naphthenate and 4-methoxybenzophenone on the degradation of LDPE [23-24]. However, the effect of 2-benzoylbenzoic acid on the degradation behavior of LDPE has not been studied.

The aim of the present work is to study the progress of photo-oxidative degradation of

LDPE films and the effect of a combination of cobalt naphthenate and 2-benzoylbenzoic acid on its degradation.

The effect of 2-benzoylbenzoic acid has also been compared with that of cobalt naphthenate, which is a conventional metallic photoinitiator, however, the combined effect of 2-benzoylbenzoic acid and cobalt naphthenate has not been investigated.

UV-irradiated LDPE films containing cobalt naphthenate, 2-benzoylbenzoic acid and a combination of both were performed and the physico-chemical changes were monitored by measuring the carbonyl index (CI), tensile strength, elongation at break, density and crystallinity.

2- Experimental

2.1- Material

The material used in this study was LDPE film grade (grade B1), with a melting flow index of 1.7 g/10 min. at 190 °C from Bandar Imam Petrochemical Company (Iran), cobalt naphthenate ($C_{22}H_{14}O_4Co$) and 2-benzoylbenzoic acid ($C_{14}H_{10}O_3$) were purchased from Fluka Co. (Germany) and were used without further purification.

2.2- Preparation of the films

Sheets of 2.0 mm thickness were prepared by press-moulding which was carried out at 170°C [25] with different concentrations of LDPE, cobalt naphthenate and 2-benzoyl benzoic acid.

Table 1 shows the formulations of the samples.

2.3- Irradiation of the films

Three UV lamps each of 15-W and with a wavelength 280-400 nm were used to irradiate the films in a UV-cabinet. The distance of the sample from the light source was 30 cm and the temperature inside the cabinet was $30 \pm 1^\circ\text{C}$. The samples were taken after irradiation at regular intervals of 0, 30, 60 and 90 days, respectively, to evaluate the effect of irradiation time on degradation.

It is worth mentioning that the selection of 30 days of intervals was due to obvious detectable change by UV irradiation. Although some pre experiments in different intervals such as 10, 20 and 30 days have been done to settle the right experimental procedure, below 30 days of intervals no obvious change was detected by FTIR

spectroscopy.

2.4- Characterization

Characterization for each sample was done before and at 30-day intervals during irradiation. FTIR spectrometer, Bruker, model Equinox 55 equipped with ZnCe prism and with an incident angle of 45° was used to record the ATR-IR absorption spectra to investigate the structural changes upon exposure. The scanned wave number range was $4000\text{--}650\text{ cm}^{-1}$.

Evaluation of the photodegradation by ATR-IR was done by following the increase in the carbonyl absorbance peak around 1715 cm^{-1} during irradiation. The peak at 1465 cm^{-1} was used as a reference peak or internal standard. The results were expressed by carbonyl index defined as $A_{1715}/A_{1465\text{cm}^{-1}}$ [26, 27].

$$\text{Carbonyl Index (CI)} = \frac{\text{Absorption at } 1715\text{ cm}^{-1} \text{ (the maximum of carbonyl peak)}}{\text{Absorption at } 1465\text{ cm}^{-1} \text{ (internal standard)}} \quad (1)$$

Table 1. Formulations and designation of the samples

| Sample | LDPE% (w/w) | Cobalt naphthenate % (w/w) | 2-benzoylbenzoic acid % (w/w) |
|--------|-------------|----------------------------|-------------------------------|
| PE | 100 | 0 | 0 |
| PEB1 | 99.95 | 0 | 0.05 |
| PEB2 | 99.90 | 0 | 0.10 |
| PEB3 | 99.85 | 0 | 0.15 |
| PEB4 | 99.80 | 0 | 0.20 |
| PECB1 | 99.90 | 0.05 | 0.05 |
| PECB2 | 99.85 | 0.10 | 0.05 |
| PECB3 | 99.80 | 0.15 | 0.05 |
| PECB4 | 99.75 | 0.20 | 0.05 |

Tensile properties of the samples were measured by MTS Instrument model 10/M (USA). Sheets of 2.0 mm. thickness and 75 mm. lengths and 5 mm. widths were cut off for exposure. The tests were performed on the samples according to ASTM D 638-03 S. The samples were subjected to cross-head speed of 100 mm/min. The test was undertaken in air conditioned environment at $23 \pm 0.5^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. Five samples were tested for each experiment and the average value was reported. NETZSCH DSC 200 F3 thermal analyzer instrument (Germany) was used to measure the relative crystallinity of the samples in a closed Al pan. The calibration method was manual and the pressure of the inlet gas was 5 bars, with a flow rate of 50 ml/min. under N_2 atmosphere. The samples were heated up to 150°C at a rate of $10^\circ\text{C}/\text{min.}$, held at this temperature for 5 min., then cooled to 55°C at $-10^\circ\text{C}/\text{min.}$ to eliminate thermal history. The melting and crystallization behaviors were taken from the second heating and cooling cycles. The relative crystallinity of samples to the crystallinity of pure LDPE was calculated assuming that the heat of fusion of pure LDPE was 290 J/g. [28]. A 6

column density instrument (Davenport-England) was used to measure the changes in the apparent density. The measurements were done according to ASTM D 1505 at $23 \pm 0.1^\circ\text{C}$ and 31% relative humidity.

3- Results and discussion

In this work the effect of cobalt naphthenate and 2-benzoylbenzoic acid on the rate of degradation of low density polyethylene films were studied. The hypothesis to expect any effect of benzoylbenzoic acid on LDPE degradation is drawn from the literature as aromatic ketones have effective photoinitiation on several polymers [22].

3.1- FTIR Spectroscopy analysis

Figures 1 and 2 show the FT-IR spectra of LDPE films containing cobalt naphthenate and 2-benzoylbenzoic acid.

In the FTIR spectra of the samples, there are significant changes observed in the carbonyl ($1710\text{--}1730\text{ cm}^{-1}$), (C-H) (1300 cm^{-1}) regions, (bending vibration, when CH_3 is attached to C atom). This information indicates that the oxidation or degradation has occurred in these samples.

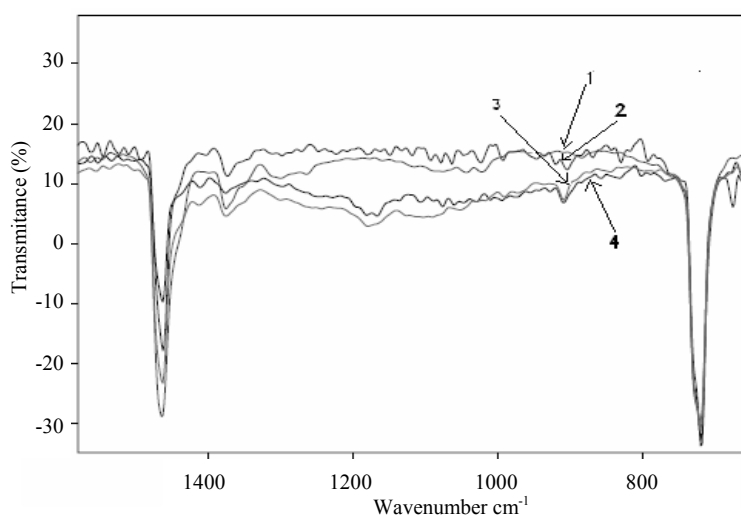


Figure 1. FTIR spectra of LDPE films (sample PECB4) during UV photooxidative degradation. Numbers on curves indicate UV irradiation time in days (1) 0, (2) 30 (3) 60 and (4) 90 days

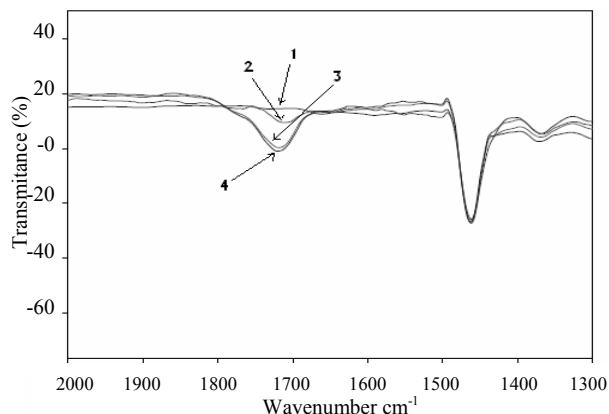


Figure 2. The normalized FTIR spectra of LDPE films (sample PECB4) during UV photooxidative degradation. Numbers on curves indicate UV irradiation time in days (1) 0, (2) 30 (3) 60 and (4) 90 days

By comparing the FTIR spectra of different irradiated films, it is observed that the degradation rate of the irradiated films increases when the concentration of cobalt naphthenate increases, as well as increasing the time of irradiation, but incorporation of 2-benzoylbenzoic acid retarded the rate of degradation.

The characteristic peak of PE at 1465cm^{-1} was normalized for all the spectra and the area under peak for this region was calculated as well as the area for the region $1715\text{-}1730\text{cm}^{-1}$ [29], and the carbonyl index for the samples. It was clear that at 0 day irradiation time, no considerable progress in oxidation reaction or degradation can be observed. But after 30, 60 and 90 days, there is an obvious change in the corresponding peak which indicates the increase in the degradation rate with time. Figure 3 shows the plot of CI as a function of time in LDPE and LDPE containing varying amounts of cobalt naphthenate and varying amounts of 2-benzoylbenzoic acid. We found that 2-benzoylbenzoic acid retarded the photooxidative degradation of LDPE and the carbonyl index of pure LDPE increased from

1.75 to 2.75 after 30 days, reaching up to 12.64 after 90 days on exposure to UV-irradiation. This will be 0.52 to 1.42 after 30 days and 5.27 after 90 days for PE containing 0.10% 2-benzoylbenzoic acid and 0.03 to 0.08 up to 0.84 for the same series of PE containing 0.10% cobalt naphthenate and 0.05% 2-benzoylbenzoic acid. This means that incorporation of 2-benzoylbenzoic acid into the polymer led to a significant decrease in the CI in the same series. That is, increasing the concentration of 2-benzoylbenzoic acid retarded the degradation. Similar results for keto acidic compounds have been reported by Jahanmardi and Assempour[30].

Although there is a retardation effect for increasing the concentration of 2-benzoylbenzoic acid, increasing the concentration of cobalt naphthenate leads to an increase in the rate of degradation.

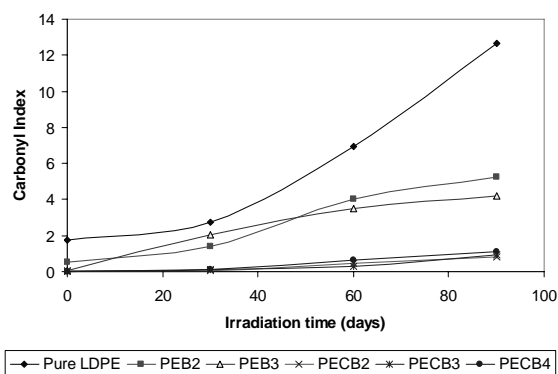


Figure 3. Effect of cobalt naphthenate and 2-benzoylbenzoic acid on the photooxidation of LDPE films.

3.2- Mechanical properties

The effect of concentrations of cobalt naphthenate and 2-benzoylbenzoic acid on the tensile strength and elongation at the break of LDPE films are presented in Figs. 4 and 5.

It can be seen that there is a decrease in the tensile strength and elongation at the break of samples when the amount of sensitizer increases, as well as increasing the time of irradiation. The decreasing rate of elongation at break for all samples was very fast during the first 30 days of irradiation compared with the second and third months of irradiation.

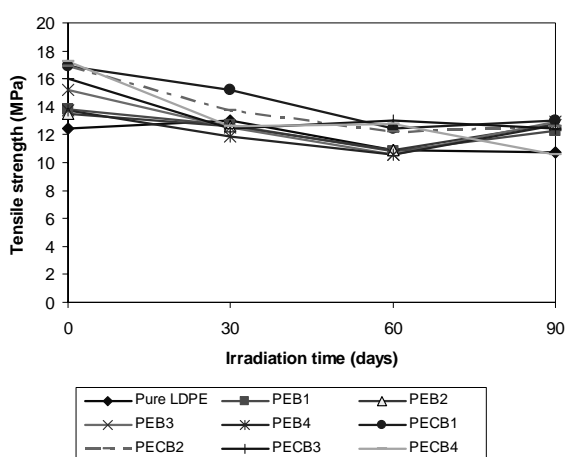


Figure 4. Changes in tensile strength of LDPE films with varying amounts of 2-benzoylbenzoic acid and varying amounts of cobalt naphthenate

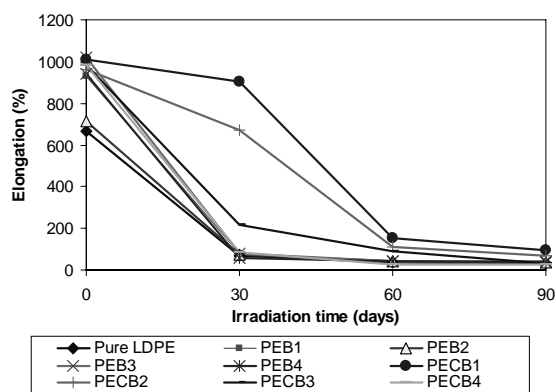


Figure 5. Changes in elongation at break of LDPE films with varying amounts of 2-benzoylbenzoic acid and varying amounts of cobalt naphthenate.

The main reason for the decrease in tensile and elongation at break is that the polymer chains in the presence of sensitizer take up oxygen and this leads to the formation of hydroperoxides which break down to give

lower molecular weight oxygenated products, which can be detected by FTIR spectroscopy. The rate of decrease in tensile strength (Table 2) for the samples containing cobalt naphthenate and 2-benzoylbenzoic acid are calculated according to the following equation:

$$\text{Rate of decrease in tensile strength} = \Delta (\text{tensile}) / \Delta t$$

Table 2. Rate of decrease in tensile strength of PE samples and samples containing 2-benzoylbenzoic acid and cobalt naphthenate.

| Sample | Rate of decrease in tensile strength (Mpa/day) | | |
|--------|--|--------------------------|--------------------------|
| | R ₁ (30 days) | R ₂ (60 days) | R ₃ (90 days) |
| PE | 0.02 | 0.07 | 0.007 |
| PEB1 | 0.04 | 0.06 | 0.05 |
| PEB2 | 0.03 | 0.06 | 0.06 |
| PEB3 | 0.09 | 0.06 | 0.08 |
| PEB4 | 0.06 | 0.04 | 0.07 |
| PECB1 | 0.06 | 0.09 | 0.02 |
| PECB2 | 0.11 | 0.05 | 0.01 |
| PECB3 | 0.12 | 0.02 | 0.02 |
| PECB4 | 0.15 | 0.007 | 0.07 |

The results presented in Table 2 show that the rate of decrease in tensile strength is less for neat LDPE, but greater for the sample containing cobalt naphthenate and 2-benzoylbenzoic acid. The rate of decrease in tensile strength is also greater for the samples containing cobalt naphthenate alone. This means that 2-benzoylbenzoic acid has a retarding effect on photo-oxidative degradation while cobalt naphthenate has an accelerating effect on the degradation of LDPE.

3.3- Thermal analysis

The effect of irradiation time on relative crystallinity (R.C. %) and melting points (T_m) with varying amounts of cobalt naphthenate and 2-benzoylbenzoic acid are presented in Table 3.

Table 3. Effect of irradiation time on relative crystallinity (R.C.) (%) and melting point (T_m)

| Irradiation time | 0 (days) | | | 30 (days) | | | 60 (days) | | | 90 (days) | | |
|------------------|----------|------------|------------------------|-----------|------------|------------------------|-----------|------------|------------------------|-----------|------------|------------------------|
| | R.C. (%) | T_m (°C) | ΔH_{exp} (J/g) | R.C. (%) | T_m (°C) | ΔH_{exp} (J/g) | R.C. (%) | T_m (°C) | ΔH_{exp} (J/g) | R.C. (%) | T_m (°C) | ΔH_{exp} (J/g) |
| PE | 31.15 | 113.3 | 90.33 | 27.43 | 114.2 | 79.54 | 26.16 | 114.7 | 75.86 | 28.36 | 114.3 | 82.24 |
| PECB 1 | 30.02 | 112.2 | 87.07 | 29.66 | 112.8 | 86.00 | 28.49 | 112.7 | 82.63 | 28.70 | 115.4 | 83.24 |
| PECB2 | 29.81 | 113.5 | 86.45 | 28.87 | 115.7 | 83.72 | 26.49 | 113.3 | 76.83 | 28.66 | 114.2 | 83.12 |
| PECB 3 | 29.32 | 115.7 | 85.03 | 28.90 | 114.4 | 83.81 | 26.79 | 112.3 | 77.69 | 27.27 | 113.2 | 79.09 |
| PECB 4 | 30.03 | 113.2 | 87.09 | 28.40 | 112.9 | 82.37 | 28.10 | 117.7 | 81.50 | 32.87 | 112.8 | 95.31 |

The degree of crystallinity was calculated using the equation:

$$\% \text{ crystallinity} = (\Delta H_{exp} / \Delta H^\circ) 100 \quad (2)$$

Where ΔH_{exp} is the experimentally determined heat of fusion and ΔH° is the heat of fusion of the completely crystalline polyethylene (290 Jg^{-1}) measured at the equilibrium melting temperature [28, 31].

Figure 6 shows a typical DSC analysis for a sample of LDPE. The degree of crystallinity of LDPE films versus irradiation time for samples with 0.05% 2-benzoylbenzoic acid and different concentrations of cobalt naphthenate has been shown in Fig. 7.

This figure shows little change in the crystallinity of the samples during the course of photo-oxidation via UV irradiation. From the DSC melting endotherms data it was seen that there is a slight change in T_m (melting point) with increasing the time of irradiation. From this it can be concluded that the initial degradative changes took place in the amorphous regions of the polymer, leaving the crystalline regions unaffected. The slight changes in the amount of the heat of fusion can be attributed to few changes in crystallite sizes and molecular weight reduction due to

chain breaking and secondary crystallization, which occurred because of chain scission.

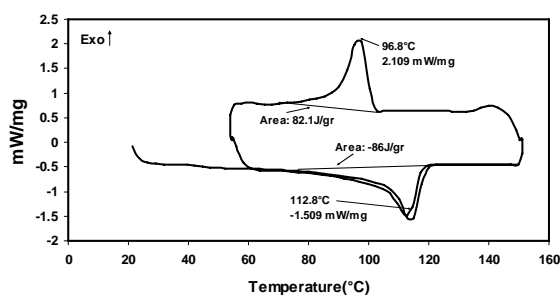


Figure 6. A typical DSC. Analysis showing ΔH_{exp} . For sample PECB 1 after 30 days

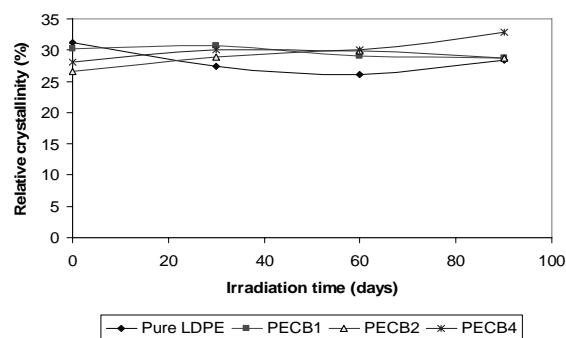


Figure 7. The Effect of irradiation time on the relative crystallinity (R.C. %) of LDPE films with 0.05 wt. % 2-benzoylbenzoic acid and varying amounts of cobalt naphthenate

3.4- Density measurement

Figure 8 shows the effect of irradiation time and concentrations of cobalt naphthenate and

2-benzoylbenzoic acid on the density of LDPE films. The density increased after UV irradiation by increasing the time of exposure. The reason for this is that the oxidations of polyethylene increase the density during the aging process [32] because during the process of degradation the material becomes denser due to the firmer packing and incorporation of oxygen into the amorphous region of the polymer, and so the polymer become thicker [26].

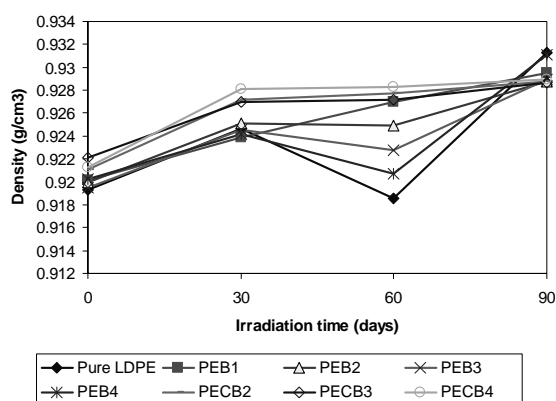


Figure 8. Effect of irradiation time on the density of LDPE films with varying amounts of cobalt naphthenate and varying amounts of 2-benzoylbenzoic acid

The density of all the samples increased over a period of 90 days of UV exposure. The increase in density was more in the case of films containing cobalt naphthenate compared to neat polyethylene and polyethylene containing both cobalt naphthenate and 2-benzoylbenzoic acid. This is due to the retardation effect of the 2-benzoylbenzoic acid.

4- Conclusions

The effect of the combination of cobalt naphthenate and 2-benzoylbenzoic acid on the photo-oxidation degradation of low

density polyethylene was studied.

The FTIR measurements show that there is a noticeable change in the carbonyl region, which means that the degradation happened to these samples. From the results it was clear that the degradation rate of the irradiated films increases in the samples containing cobalt naphthenate only, but by incorporation of 2-benzoylbenzoic acid the degradation rate decreased. The combination of cobalt naphthenate and 2-benzoylbenzoic acid shows a decrease in the mechanical properties (tensile and elongation), this is because the oxygen taken by the polymer leads to the formation of hydro peroxide which break down to give low molecular weight oxygenated products. The decrease in tensile strength and elongation at the break for the samples containing 2-benzoylbenzoic acid was only less than that for neat LDPE film and LDPE films containing cobalt naphthenate and 2-benzoylbenzoic acid. This is because of the retarding effect of the 2-benzoylbenzoic acid.

DSC measurements show slight changes in the crystallinity of the samples, which means that the initial degradative changes took place in the amorphous regions of the polymer without affecting the crystalline regions.

Density measurements show that the increase in the density was higher in films containing cobalt naphthenate compared to neat LDPE films or to films containing LDPE and cobalt naphthenate and 2-benzoylbenzoic acid.

From the results of the FTIR measurements, mechanical properties, thermal analysis and density it was concluded that the rate of UV degradation increased when the concentration of cobalt naphthenate was

increased, as well as the time of irradiation but incorporation of 2-benzoylbenzoic acid retarded the rate of degradation.

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