EFFECT OF CaCO₃ FILLER ON THE DEGRADATION OF HIGH DENSITY POLYETHYLENE (HDPE) FILM CONTAINING PROOXIDANTS

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ABSTRACT

The aim of this work is investigation of effect of CaCO₃ filler on the degradation of high density polyethylene (HDPE) films containing stearate salts as prooxidant additives. The films with thickness of 30 μm were prepared by adding 0.3 wt % prooxidant additives mixture (manganese (II) stearate/ferric stearate/cobalt (II) stearate with ratio of 18:4:1) and CaCO₃ filler from 5 to 20 wt % to HDPE resins by using twin screw extruder. The films were subjected to accelerated weathering treatment according to ASTM G154 standard (340 nm UV lamp, 8 hours UV, 4 hours condensation at 50 °C) for maximum duration of 96 hours. The mechanical properties, Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and scanning electron microscope (SEM) were used to assess the changes of films during accelerated weathering. The results showed that the degradation rate of HDPE films with CaCO₃ filler is slower than that of HDPE without CaCO₃ filler, but the higher the CaCO₃ content is, the faster degradation rate HDPE is. After 96 hours of accelerated weathering treatment, the elongation at break of the HDPE film with 5 % CaCO₃ almost unchanged while this value of the HDPE films with 10 and 20 % CaCO₃ decreased significantly (96 % and 100 %, respectively). FTIR spectra of HDPE films with 10 and 20 % CaCO₃ showed carbonyl group’s peak as the result of oxidation. FTIR spectra also indicated that CaCO₃ filler did not affect to the mechanism of polyethylene degradation.

Keywords: calcium carbonate, filler, polyethylene degradation, accelerated weathering.

1. INTRODUCTION

Polyethylene is the most widely used semicrystalline material in the world, especially in the packaging industries. HDPE has many advantages such as good flexibility and chemical resistance, low cost, high impact and toughness strength [1], so it is the most commonly used plastics among the polyethylene family. However, like other polyolefins, they are very difficult to be biodegraded in the natural environment. In the past few decades, the scientists tried to
promote biodegradation of the conventional polyolefin materials, especially polyethylene by using pro-oxidants. Prooxidant additives are usually transition metal ions (such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ca ...) introduced in the form of complexes with other organic compounds. These additives will promote the degradation of polyethylene producing polar functional groups such as carboxylic acid, alcohol, aldehyde, ketone, ester, etc. [2].

In recent years, the incorporation of inorganic mineral powder into plastics has been particularly interested because they help to reduce the product costs, the white pollution, and thus to protect the environment. Calcium carbonate is the most commonly used filler in the plastic industry, the largest amount of inorganic (accounting for more than 70%) because it has many advantages such as availability, low cost, good stability, pure color, low wear, easy to dry and to process, non-toxic, etc. Today, CaCO₃ filler plays a role preferably in polyethylene based films and sheets. Several studies were published recently, but they focused on preparation, characterization and thermal degradation of CaCO₃ filled composites. Kamil Şirin studied mechanical and thermal properties of PP-LDPE and PP-LDPE/DAP composites with different CaCO₃ contents [3]. The preparation and characterization of LDPE/CaCO₃ nanocomposites were studied by Wang et al. [4]. Thai Hoang et al. reported that CaCO₃ can promote the hydrolysis of PLA/EVA/CaCO₃ composites in base solution and sludge environment [5]. Our previous studies indicated that prooxidants promoted thermo and photo-oxidation of PE films [6, 7]. In this paper, effect of different CaCO₃ filler contents on the degradation of high density polyethylene (HDPE) film containing prooxidants was studied.

2. MATERIALS AND METHODS

2.1. Materials

HDPE F00952 manufactured by Saudi Basic Industries Corporation (Saudi Arabia), had density 0.952 g/cm³, melt flow index (MFI) of 0.05 g/10 min at 2.16 kg/190 °C. Cobalt (II) stearate, manganese (II) stearate and ferric stearate were supplied by Jingjiang Hangsun Plastic Additives Co., Ltd (China). These additives were introduced into the PE matrix in the form of a masterbatch (10 wt % of prooxidants mixture, manganese/ferric/cobalt stearate with weight ratio of 18:4:1). Calcium carbonate (CaCO₃) filler with an average particle diameter of 3µm was supplied by HP Company, Hai Phong, Vietnam.

2.2. Sample preparation

In this study, HDPE films were made by extrusion blowing by using a XD 35 extruder with a 35 mm screw of L/D 28:1. These films with a thickness of 30 µm contain 0.3 wt % prooxidant additives (equivalent to 3 % prooxidant masterbatch) and different CaCO₃ filler contents (0, 5, 10 and 20 % - symbol HD3, HD53, HD103, HD203, respectively).

2.3. Accelerated weather testing

The accelerated weathering was carried out in a Ultraviolet/Condensation Screening Device (UVCON) Model UC-327-2 according to ASTM G154 standard. The 7 × 14 cm HDPE films were tested under accelerated conditions (340 nm UV lamp, 8 hours UV at 70 °C, 4 hours condensation at 50 °C) for 96 hours.
2.4. Tensile tests

Tensile testing was carried out on an Instron 550 according to ASTM D882 at a cross-head speed of 10 mm/min. All the test samples were conditioned at 23 °C and 50 % relative humidity (RH) for 24 h before testing.

2.5. FTIR studies

A Fourier transform infra-red (FTIR) spectrometer (NEXUS 670) was used to obtain the IR spectra. The equipment was operated with a resolution of 4 cm⁻¹ and scanning range from 4000 to 400 cm⁻¹.

2.6. Thermal analysis

Thermogravimetry analysis was carried out at 10 °C/min heating rate in air, from room temperature to 600 °C on thermogravimetry analysis system (Setaram 1600).

2.7. Surface morphological studies

A scanning electron microscope SM-6510LV (JEOL – Japan) was used to study the morphology of the samples. Samples were sputter-coated with platinum before scanning.

3. RESULTS AND DISCUSSIONS

3.1. Mechanical properties

Tensile strength and elongation at break of original and photo-oxidised HDPE films containing CaCO₃ and prooxidants are presented in Table 1.

*Table 1. Changes in mechanical properties of HDPE films containing CaCO₃ and prooxidants.*

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HD3</td>
<td>HD53</td>
</tr>
<tr>
<td>Origin</td>
<td>30.3</td>
<td>24.7</td>
</tr>
<tr>
<td>24 hours</td>
<td>24.6</td>
<td>24.4</td>
</tr>
<tr>
<td>48 hours</td>
<td>16.9</td>
<td>24.7</td>
</tr>
<tr>
<td>72 hours</td>
<td>6.4</td>
<td>24.4</td>
</tr>
<tr>
<td>96 hours</td>
<td>2.5</td>
<td>24.6</td>
</tr>
</tbody>
</table>

The results showed that all HDPE films containing CaCO₃ were degraded more slowly than HD3 film after photo-oxidation. This may be due to thermal stabilization effect of CaCO₃ filler [8]. Similarly, Rui Yang [9] studied the thermal oxidation of composites of polyethylene and inorganic fillers such as diatomite, kaolin, calcium carbonate, talc, mica, wollastonite...and also found that CaCO₃ filler retarded the thermal oxidation of HDPE. They suggested that diatomite, wollastonite and calcium carbonate may be used as potential antioxidants. In addition, CaCO₃ can retard photo-degradation of HDPE films because it is capable of reflecting nearly all the ultraviolet light [10].

However, when increasing amount of CaCO₃, the stabilization effect is reduced. The mechanical properties of HDPE film containing 5 % CaCO₃ unchanged after 96 hours of UV exposure, these value of film containing 10 % CaCO₃ began to decrease after 24 hours. However, the mechanical properties of film containing 20 % CaCO₃ decreased as soon as
exposure to UV and was completely degraded after 72 hours. This implied that low CaCO₃ filler concentrations (< 5%) exhibited a better antioxidant role than high concentrations (> 10%). It is possible that at low concentrations, the CaCO₃ filler dispersed in the polyethylene matrix better than at high concentrations. At high concentrations, the CaCO₃ filler dispersed not well in PE matrix caused defects on the films. At the same time, CaCO₃ increases the gas permeability of films so oxygen which causes oxidation reaction, easily penetrated.

3.2. FTIR-spectroscopy

FTIR spectra of original and photo-oxidized films were shown in Figure 1 and 2, respectively.

![Figure 1. FTIR spectra of original HDPE films containing CaCO₃ and prooxidants.](image1)

![Figure 2. FTIR spectra of HDPE films containing CaCO₃ and prooxidants after 96 hours of photo-oxidation.](image2)

Similar to HDPE film without CaCO₃, after 96 hours of photo-oxidation, FTIR spectra of HD103, HD203 films show the peaks in the range of 1700 – 1800 cm⁻¹ for carbonyl groups which are attributed to various oxidation products namely, aldehyde or ester (1733 cm⁻¹), acid
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carboxylic (1700 cm⁻¹), γ-lacton (1780 cm⁻¹). In addition, FTIR spectra of original and oxidized HD103, HD203 films also show peak at 1795 cm⁻¹ which was assigned to C=O of CO₃²⁻ group in CaCO₃ molecule [11]. This confirms that CaCO₃ may change the degradation rate, but it may not change the degradation mechanism of HDPE film. The results are consistent with research of Rui Yang et al. [9].

The results also showed that, FTIR spectra of original and photo-oxidized HD53 film were not different. This is a proof that HD53 is not oxidized after 96 hours. The intensity of the 1714 cm⁻¹ peak of the HD203 film is stronger than of HD103 film, this indicates that HD203 film is more degraded than HD103 film.

3.3. Thermal analysis

The thermal analysis curves of original and photo-oxidized HDPE films with CaCO₃ are shown in Figure 3. The temperature at which a sample loses 5% of its weight (T₅) was used as decomposition onset temperature. Analysis data from the thermal analysis curves of HDPE films with CaCO₃ and prooxidants are listed in Table 2.

![Figure 3. TG and DTA curves of HDPE films containing the different amounts of CaCO₃.](image)

Table 2. Thermal analysis value of HDPE films containing CaCO₃ and prooxidants.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Original</th>
<th>96 hours of photo-oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T₅ (°C)</td>
<td>Weight loss (%)</td>
</tr>
<tr>
<td>HD3</td>
<td>347.3</td>
<td>99.2</td>
</tr>
<tr>
<td>HD53</td>
<td>330.6</td>
<td>89.2</td>
</tr>
<tr>
<td>HD103</td>
<td>393.1</td>
<td>86.3</td>
</tr>
<tr>
<td>HD203</td>
<td>395.2</td>
<td>78.2</td>
</tr>
</tbody>
</table>

After 96 hours of photo-oxidation, similar to film without CaCO₃ melting temperature of HD103, HD203 films is lower than that of original film, while these values in HD53 are almost unchanged. However, heat of fusion of HDPE film without CaCO₃ increases but heat of fusion of HDPE films with CaCO₃ decrease. The melting point reduction increases in the order HD103 (ΔH = 5.0) < HD203 (ΔH = 8.8) < HD53 (ΔH = 24.3). The results also show that TA curves for all the films exhibits one stage decomposition and T₅ of photo-oxidized HDPE films after 96
hours is lower than of original films, especially HD103 and HD203. This indicated that these films degraded to shorter chains.

3.4. Surface morphology of HDPE films

![Figure 3. SEM micrographs of original HDPE films: (a) HD3, (b) HD53, (c) HD103, (d) HD203.](image1)

![Figure 4. SEM micrographs of HDPE films after 96 hours of photo-oxidation: (a) HD3, (b) HD53, (c) HD103, (d) HD203.](image2)

Figure 4 and 5 showed the surface morphology of HDPE films containing CaCO₃ and prooxidant additives before and after photo-oxidation, respectively.
The results showed that original HD3 films presented a smooth surface with free of defects while the surfaces of photo-oxidized HD3 film showed a pronounced roughness. Due to roughness surface of original film containing CaCO₃, it is much more difficult to observe the changes of film surface after the oxidation. Surface morphologies of HD53 and HD103 films were almost no change while HD203 surface has more craters. The SEM image also showed that CaCO₃ filler in HD103 and HD203 films is agglomerated to form defects on the film surface. Yang et al [12] also found that inorganic fillers such as diatomite damage the film surface when added to the film, that results in faster degradation of HDPE.

4. CONCLUSIONS

The degradation of HDPE films containing CaCO₃ and prooxidant additives was studies by accelerated weathering test. CaCO₃ filler retards the degradation of HDPE films containing prooxidants by prolonging the induction phase of the degradation of HDPE films but they don’t affect to the mechanisms of degradation. FTIR spectra of HD103, HD203 films after 96 hours of exposure to UV showed the presence of the polar functional groups such as aldehyde, ester, carboxylic acid, etc. It was observed that HDPE films with > 5 % CaCO₃ were more quickly degraded than that with < 5 % CaCO₃.

REFERENCES


