6.0 Introduction

The wide usage of polyethylene (PE) in packaging industry has become inevitable owing to its advantage of flexibility, physical strength, durability and frugality. Polyethylene (PE) plays a vital role in packaging food stuff, preparing tetra-packs, candy wafers, shampoo sachets, motor pumps and other equipment sealing covers, etc (Moura et al., 2004). Over a period of usage it has become one among the materials of municipal garbage. Aerobic composting is being supported as a major effort to dispose waste. Still landfill remains the major waste management method globally (Telmo et al., 2009; Scott, 2000). PE is relatively inert due to its hydrophobic chains and high molecular weight. From earlier studies, it is evident that polyethylene biodegrades less than 0.5% in 100 years and about 1% if pre-exposed to sunlight for about 2 years (Khabbaz et al., 2001). PE represents a significant percentage of municipal waste. The cost of collecting, cleaning and sorting the entire post-consumer PE is high, and the market for mechanically recycled PE is limited.

Researchers adopted many new methods to facilitate the environmental abiotic-oxidation and biodegradation of PE by polymer copolymerization (Otey et al., 1987), grafting and blending with oxo-biodegradable additives (Kemp et al., 2006; Roy et al., 2006) or direct incorporation of natural biodegradable polymers, such as starch (Piyush et al., 1995; Anthony et al., 1992). Oxo-biodegradable additives consisting of parts per million levels of transition element/metal organic salts added to conventional plastics like polyethylene (PE) and polypropylene (PP), are used to make polyolefin plastic degrade rapidly when it reaches end-of-use. Iron acts as a “delayed action” photo-sensitizer (Wiles and Scott, 2006) activated by
UV light exposure, whereas Ni, Cr (IV), Co and Cu (Roy et al., 2009; Gorghiu et al., 2004; Bheki et al., 2009) are sensitive to thermal activation. The transition metals can exhibit variable oxidation states and it is responsible for their pro-oxidant nature. The central metal responsible for the pro-oxidative ability usually belongs to the first transition series like manganese, iron and cobalt as stearates, all of which have the capacity to exist in both +2 and +3 oxidation states (Roy et al., 2009).

The manufacturers normally don’t reveal the identity of the pro-oxidant additive(s) used in commercial oxo-biodegradable additives. But the modifications they induce in the polymer’s functional behaviour are quite interesting. The additives are probably based on transitional metals, capable of yielding two metal ions differing in the oxidation number by one unit (Andrea et al., 2010). The pro-oxidants help to generate free radicals, which react with molecular oxygen to produce peroxides, hydro-peroxides and lead to PE decomposition under light and heat conditions leading to the formation of ketones and olefins. (Lee et al., 1991; Khabbaz et al., 1991). It facilitates chain end session and random session of PE via classical free radical chain reaction. (Jakubowicz, 2003; Gugumus, 2001).

The present chapter investigates the changes in the mechanical and surface of modified LDPE films upon the introduction of hydrophilic groups on the polymer surface by thermal-oxidation as influenced by a commercially available oxo-biodegradable additive.

6.1 Experimental method

6.1.1 Preparation of low density polyethylene film

Virgin LDPE films were prepared using a film blowing machine (reported in chapter 5) using an extruder (Gurusharan Polymer Make) and LDPE film was designated as PE and films containing oxo-biodegradable additive were designated as BPE followed by a
numerical suffix indicating the amount of additive added. LDPE films containing 10% and 20% oxo-biodegradable additive were designated as BPE10 and BPE20 respectively.

6.1.2 Thermal-oxidation procedure

Oven aging

Thermal-oxidation was carried out by placing the blown films in an air oven (Matri India, [P] Ltd, India) maintained at 70°C for extended periods (Roy et al., 2009; Andrea et al., 2010). Exposures were conducted in the presence of air and the PE samples were uninterrupted, (24 hr per day). The samples were recovered in different time intervals.

6.2 Characterization techniques

6.2.1 Mechanical strength test

Changes in mechanical properties like tensile strength and elongation at break were performed on LDPE films according to ASTM 882-85 using INSTRON machine (no. 6021). Films of 100 mm length and 25 mm width made as strips were subjected to a crosshead speed of 50 mm/min. The tests were taken at air-conditioned environment at 21°C and with a relative humidity of 65%. The value is the average of five samples for each experiment.

6.2.2 Fourier transformed infrared spectroscopy (FT-IR)

The surface chemical modifications which occur in LDPE films due to thermo-oxidation were investigated using FTIR spectroscopy. The FTIR spectra were recorded using a Thermo Nicolet, Avatar 370 spectrophotometer in the spectral range between 4000-400 cm⁻¹. The keto carbonyl index was measured from the relative intensity of the keto carbonyl bond at 1720cm⁻¹ to that of the Methylene band at 1465 cm⁻¹ was evaluated using the formulae;
Keto carbonyl bond index = \( \frac{1720}{1440} \) (Sudhakar et al., 2009)

### 6.2.3 Contact angle and surface energy

Wettability determinations of film surfaces submitted to thermo-oxidation were performed by contact angle measurements on samples using a video based contact angle meter OCA 20 attached to a camera. The wetting liquid used was Millipore grade distilled water (liquid surface tension \( \gamma \) = 72.8 mJ/m²). The value is the average of five samples for each experiment.

Surface energy was calculated using equation of state, Schultz Method-2, using Data Physics SCA20 software (Version 2.01).

The adhesion work \( W_{adh} \), a quantity related to surface wettability, was calculated using the formulae; (Navaneetha et al., 2008)

\[
W_{adh} = \gamma (1 + \cos \theta)
\]

Where \( \gamma \) and \( \theta \) are surface energy of testing liquid and contact angle of the LDPE.

### 6.2.4 Morphological analysis

Changes in the surface morphology due to thermo-oxidation were investigated with SEM, (JEOL Model JSM - 6390LV) using a voltage of 15kv. Photomicrographs were taken at uniform magnification of 5000 fold and surface topography of the films were analysed by AFM (Solver P 47 PRO, Russia) using the semi-contact mode, under normal laboratory air atmosphere with the scan rate of 0.5 Hz, using single crystal silicon antimony doped probe to evaluate the change in surface topography.
6.3 Results and Discussion

6.3.1 Mechanical properties

The initial elongation at break of pristine LDPE, BPE10 and BPE20 were 727.4, 713.4 and 718.1 respectively (Figure 6.1). As the thermal-oxidation time increases, the pro-oxidant induces the chain end session (Roy et al., 2008) thereby rendering the polyethylene to lose its mechanical strength. Over a period of 35 days the pro-oxidant additive added PE retained very low value. The property of tensile strength reflects the physical strength of the polymer after a prolonged period of thermal-oxidation (Figure 6.2). The BPE20 showed a deep fall from 16.9 MPa to 9.4 MPa followed by BPE10 from 16.8 MPa to 12.6 MPa and the pristine PE loses only 2 MPa from its initial strength of 16.6 MPa. Thus the visual effect of the polymer shows “brittle” in nature.

6.3.2 Structural properties - FT-IR analysis

Structural changes resulting from thermal-oxidation were investigated by recording the FTIR spectra of films in different time periods. During thermal treatment, polyethylene undergoes oxidation by producing radicals that further propagate to form peroxides. The most significant changes in the IR absorption spectra were in the carbonyl (1,785-1,700 cm⁻¹) peak. After 20 days of thermo-oxidation an increase was observed in the intensity of the absorption band around 1720 cm⁻¹, which can be assigned to the C=O stretch of the saturated aliphatic keto-carbonyl group was observed (Khabbaz et al., 1999). In pristine PE (Figure 6.3a), the carbonyl bond is a result of the overlap of various stretching vibration bands including those of aldehydes and/or esters and carboxylic acid groups (Roy et al., 2008). The sharp peak of 1473-1446 cm⁻¹ resulted in CH3 deformation. After 10 days of thermo-oxidation the BPE10 (Figure 6.3b) shows the formation of keto carbonyl (1720 cm⁻¹) groups. It reaches maximum only after 35 days. The spectra also reveals the over lapping of primary
and secondary amines. The influence of pro-oxidant is significant in spectral arrangement of BPE20 (Figure 6.3c); it sharply induces the formation of saturated aliphatic keto-carbonyl functional groups upon prolonged thermo-oxidation. In the near regions, n-alkane and the secondary nitroalkane formation overlap each other causing a broadening of the peak; CH₃ deformation was deemed responsible for C-H scissoring (Baljit Singh and Nisha Sharma, 2008). The peak intensity of C=O stretching at the keto-carbonyl functional group (1720 cm⁻¹) and ester group (1748 cm⁻¹) increases with prolonged thermo-oxidation (Khabbaz et al., 1999; Sudhakar et al., 2007; Roy et al., 2008).

The extent of degradation has been quantified by calculating the CI, which is the intensity of \( \frac{I_{1720}}{I_{1468}} \) cm⁻¹ (Roy et al., 2008). The table 6.2, presents the variations in CI as a function of thermo-oxidation and the time period of exposure. It is evident that, only a small value increased in CI of pristine PE, but the BPE10 and BPE20 showed a gradual increase. The added pro-oxidant can manifest the changes in introducing the new functional groups to the BPE10 and BPE20.

6.3.3 Surface wettability

**Contact angle, adhesion work and surface energy measurements**

The thermo-oxidation modifies the PE and BPE samples property of surface wettability. The decrease in contact angle (Figure 6.4) indicates that the surfaces of the polymers have turned hydrophilic. The initial value of PE, BPE10 and BPE20 were 102.08, 105.98 and 106.78 were reduced to 91.22, 75.97 and 51.59 respectively. Upon the absorption of heat-energy, the components present in the pro-oxidant additive form free radicals. These species can combine with oxygen from air to generate polar groups, such as –OH, C=O, COOH and COO-, on the main chain of the polymer matrix. This leads to chain end session
or random session in LDPE, which alters the hydrophobic nature of the surface (Bikaris et al., 1997). This phenomenon was relatively slower in PE films without a pro-oxidant additive.

The surface energy value (Figure 6.5) rises as a function of thermal-oxidation period and concentration of pro-oxidant additive. The surface energies of untreated PE, BPE10 and BPE20 films were 21.78 mJ/m², 19.44 mJ/m² and 18.97 mJ/m², respectively. After thermo-oxidation, the surface energy of samples increases to 28.88 mJ/m², 38.17 mJ/m² and 51.59 mJ/m², respectively. The surface roughness is one of the important factors influencing the contact angle value. Wenzel was the first to discover the influence of surface roughness on contact angle. He reported that a decrease in surface roughness produces an increase in contact angle (Wenzel, 1936). The adhesion work \( W_{\text{adh}} \) of pristine PE and LDPE with a pro-oxidant additive added is presented in Table 6.3. The \( W_{\text{adh}} \) was calculated from contact angle measurements with respect to water. It increases showing the modification of surface chemical groups rendering the hydrophobic nature to hydrophilic.

6.3.4 Surface morphological and topographical analysis: SEM and AFM

Scanning electron microscopy was used to investigate the changes in the surface morphology of thermo-treated and untreated films. Figure 6.6, shows the SEM micrograph of untreated PE, BPE10 and BPE20 films. Figure 6.6.A - C shows the surface morphology as smooth, without any cracks and free from defects. Figure 6.6.A1 shows the formation of smaller cracks of 379 nm size with surface peeling in PE without additive. Fig. 6.6.B1 and 6.6.C1 are the micrographs of 35 days thermo-oxidised BPE10 and BPE20 samples. They show the increase in size of cracks and grooves, according to the increase in the concentration of pro-oxidant additive. In figure 6.6.B1 the sample BPE10 shows the cracks measuring about 3.04 µm in diameter. However, the extent of damage was much pronounced in the sample Figure 6.6.C1 containing 20% additive concentration and BPE20 shows the larger groove of 17.79 µm in diameter and the deepening of the pit is more evident. Thus the
micrograph throws light on the concentration of additive that accelerates the thermo deterioration in the presence of oxygen (Andrea et al., 2010; Sudhakar et al., 2007). The evidence of increased crack size makes the polymer more brittle as the concentration of pro-oxidant additive increases. The concentration of pro-oxidant additive influences the surface modification and facilitates the surface cracks after 35 days of thermo-oxidation.

The semi-contact mode of AFM images (Figure 6.7) revealed an increase in surface roughness for all the three samples after irradiation. Primarily before the irradiation the surface roughness of PE sample (Figure 6.7.A) was 20.58 nm and there was an increase after 35 days of thermo-oxidation in virgin PE (Figure 6.7.A1) 32.37 nm. The samples BPE10 and BPE20 showed a marked increase in surface roughness from 20.25 nm and 28.56 nm (Figure 6.7.B & 6.7.C) to 59.81 nm and 155.52 nm respectively (Figure 6.7.B1 & 6.7.C1). This shows the increased peak like pinnacle structures found more in number in BPE20 than in the other two samples. The added pro-oxidant can manifest the changes by introducing the new functional groups (such as –OH, C=O, COOH and COO-) to the BPE10 and BPE20. The results are the positive signs of the influence of increased additive concentration in accelerating the process of LDPE backbone deterioration during thermo-oxidation.
Figure 6.1 Percentage elongation of PE as a function of time for each material.
Figure 6.2 Tensile strength of PE as a function of time for each material.
Figure 6.3 FTIR spectra of (a) PE, (b) BPE10 and (c) BPE20 as a function of thermal exposure period.
Figure 6.4 Comparative photographs with chart of changes in contact angle during thermo-oxidation (i) PE, (ii) BPE10 and (iii) BPE20 film as a function of various thermal exposure period.
Figure 6.5 Surface energy variation profiles of thermally oxidised PE and BPE films as a function of exposure time.
Figure 6.6 Comparative SEM micrographs showing surface morphology of (A) untreated PE, (B) untreated BPE10 and (C) untreated BPE20 film with 35 days thermo-oxidised PE (A1), BPE10 (B1) and BPE20 film (C1).
Figure 6.7 Comparative AFM images showing surface topography of untreated PE (A), BPE10 (B) and BPE20 (C) film with 35 days thermo-oxidised PE (A1), BPE10 (B1) and BPE20 film (C1).
Figure 6.8 Effective of thermo-oxidation on PE and the changes in its surface and mechanical properties.
Table 6.1 Characteristics of LDPE blown film samples used in thermal-oxidation tests

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Transparency</th>
<th>Oxo-biodegradable additives (%)</th>
<th>Polyethylene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>Transparent</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>BPE10</td>
<td>Semi-transparent</td>
<td>10</td>
<td>090</td>
</tr>
<tr>
<td>BPE20</td>
<td>Opaque</td>
<td>20</td>
<td>080</td>
</tr>
</tbody>
</table>

Table 6.2 Influence of thermo-oxidation in increasing carbonyl index

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>(Period of thermo-oxidation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 day</td>
</tr>
<tr>
<td>PE</td>
<td>2.00</td>
</tr>
<tr>
<td>BPE10</td>
<td>1.51</td>
</tr>
<tr>
<td>BPE20</td>
<td>1.24</td>
</tr>
<tr>
<td>Sample</td>
<td>0 day</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>PE</td>
<td>57.58</td>
</tr>
<tr>
<td>BPE10</td>
<td>52.78</td>
</tr>
<tr>
<td>BPE20</td>
<td>51.58</td>
</tr>
</tbody>
</table>
6.4 Summary

The present chapter reveals that the PE samples with pro-oxidant additive shows a high degree of susceptibility to thermo-oxidation. But the pristine PE sample responds to a lesser extent of thermo-oxidation in comparison with pro-oxidant added PE. As a result of thermo-oxidation, the mechanical strength also gets reduced as the function of thermal exposure time increases. The incorporation of pro-oxidant into polyethylene initiates polymer degradation by producing free radicals which react with molecular oxygen to create peroxides and hydroperoxides which in turn promotes the chain end session of polymer backbone. Owing to the introduction of new polar groups there is a sharp increase in keto-carbonyl index was recorded in BPE20, which correlates with the other wettability parameters showing increase in surface energy and decreasing contact angle (Figure 6.8). These new polar groups contribute the change in surface property from hydrophobic to hydrophilic nature. The changes in polymer surfaces are confirmed with the modifications made in surface roughness in AFM image and the larger groove formation in SEM micrograph. The changes in surface and mechanical property due to thermo-oxidation are showing good agreement with the results of other researchers worked with pro-oxidant added PE (Roy et al.,2006; Andrea et al.,2010; Roy et al.,2008 ). The thermo-oxidative degradation of the polymer in the presence of pro-oxidant was found to follow the order: 20BPE greater than 10BPE greater than PE. The oxo-biodegradable additive added PE offers a much better alternative to traditional PE – based products. Hence the PE with oxo-biodegradable additive containing pro-oxidant can be used in packaging industry and will be helpful in controlling the plastic litter management.