UV Absorption and dynamic mechanical analysis of polyethylene films

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Photooxidative processes that lead to chain scission and chain linking in polymers play an important role in polymer degradation. These processes are induced by both ultraviolet (UV) and visible light absorption. The capability of these radiations to be absorbed depends on the existence of chromophores in the polymeric material. Assessment of photodegradation data obtained from a polymer material processed in a conventional manner is of more practical use than extrapolation of data obtained from pure resin. This study reports on the absorption of ultraviolet-light by conventionally processed polyethylene (PE) films. The PE film samples were submitted to UV from fluorescent lamps at 20°C and relative humidity 40% for two hours. Transmission, reflection and emission spectra, from which absorption was inferred, were obtained with an optical spectrum analyzer. The study also reports the natural degradation under solar action of these PE films for a period of up to 150 days. Degradation was analyzed by change of the storage modulus using a dynamic mechanical analyzer instrument. Evidence of chromophoric sites was inferred from the absorption of UV light in the range 250 to 400 nm. However, the UV absorption was low in this range. The drop of storage modulus up to 150 days, averaged for the range (50 to 98°C), fit well a hypothetical polynomial of order two.

Key words: Polyethylene, ultraviolet absorption, degradation, chromophores, storage modulus.

INTRODUCTION

Ultraviolet radiation (UV) with wavelength ranging from 200 to 400 nm, initiates oxidation degradative processes and is therefore responsible for the discoloration, weathering and loss of gloss and mechanical properties (cracking) of polymeric materials (Shah et al., 2008; Singh and Sharma, 2008; Salem, 2001). The physiochemical changes which occur during photo-oxidative reactions are characterized by an increase in the concentration of oxygen-containing groups, such as peroxides and hydroperoxides, and also ketonic carbonyl groups (Choon et al., 2004; Wiles and Scott, 2006; Massey et al., 2007). These peroxides chemically attack the bonds in the polymer molecules, reducing the molecular chain lengths to a level where they can be
 consumed by microorganisms (Wiles and Scott, 2006; Mahmood and Reza, 2004; Orhan et al., 2004). Changes in the mechanical properties of polyethylene are attributed to cross linking and chain scission processes occurring during photo-oxidation of the material (Nguyen et al., 2000). The formation of chemical functional groups in polyolefins and their role in polymer chain-breaking has been reported. These studies showed that the degradative process starts with free radical formation followed by repeated oxidation and hydroperoxides formation which leads to polymer chain breakages (Singh and Sharma, 2008; Wiles and Scott, 2006). For instance, it was found that alkyl radicals e.g. (-CH₂-CH₃) may be formed in low density polyethylene (LDPE) films during UV-irradiation (Sarathi et al., 2003). Formation of oxy-radicals and chain scission is more likely for lower wavelengths (higher energy) but also possible for wavelengths greater than 300 nm (Corales et al., 2001; Basfar and Ali, 2006). Thus, UV radiation energy effects are evident when there is a probability of its absorption. The energy is related to wavelength by the simple formula:

$$E = \frac{hc}{\lambda}$$

Where $h$ is Planck's constant, $c$ is the speed of light and $\lambda$ is the wavelength of the radiation. This gives the energy of one photon. Multiplying by Avogadro's number gives the energy for a mole of photons. The average bond energy of the carbon-carbon bond along a polymer backbone is 351 kJ/mol (Ranby and Rabek, 1975). Therefore, using the equation for energy and considering one mole of photons, 341 nm becomes the threshold wavelength where the energy is sufficient to cause chain scission of the C-C backbone. Any wavelength that is below 340 nm is capable of causing main chain backbone breakages. Table 1 gives the bond dissociation energies of various bonds of interest in polymers and the corresponding wavelengths that can cause scission.

However, most polymers containing C-C, C-H, C-O, C-N or C-Cl bonds have been reported to require a wavelength below 190 nm for appreciable formation of free radicals and subsequent photolysis (Hrdlovic, 2000). This is most likely due to steric effects of nearby chains, which assist in holding the bonds together by the close packing in a solid polymer, thus decreasing the rate of free radical formation (Hrdlovic, 2000). The portion of the sunlight-spectrum that reaches the earth’s surface is limited. Most of the higher energy X-rays, gamma rays, and cosmic rays never make it through the atmosphere due to their absorption by ozone, leaving only UV, visible, and infra red (IR) rays. Ozone absorption even takes care of the highest energy UV radiation, blocking radiation below 290 nm. The solar energy that reaches the surface is limited to the wavelength range 290 to 2450 nm. The total radiant solar energy consists of (in order of increasing energy): 37.8% IR (800-2450 nm), 55.4% visible light (400-800 nm), and 6.8% UV light (290-400 nm) (Ranby and Rabek, 1975). Polyethylene free from impurities and defects is, therefore, expected to not be susceptible to degradation under natural solar radiation since sufficiently low wavelengths do not make it to the earth’s surface. Ultraviolet-absorbing impurities (chromophores) in a polymer are what enable photolysis with wavelengths greater than 290 nm (Hrdlovic, 2000; Kroschwitz, 1990). Thus photo-degradation (either photolysis or photo-oxidation) of a material is determined by the absorption characteristics of radiation in that material (Nguyen et al., 2002). Polymeric materials are often manufactured using extrusion, injection molding, or extrusion blowing. The processing of polymers using heat and high shear to produce useful end products introduces impurities and reaction products that make them susceptible to UV radiation absorption and damage (Gowariker et al., 1988; Kroschwitz 1990; Global, 2008). Example of such impurities includes peroxides and hydroperoxides that are always formed during processing (Billingham et al., 2009; Gugumus, 2005; Kulikov and Hornung, 2004). Physical surface defects, e.g. fractures and fissures, are also known to occur during manufacture (Kulikov and Hornung, 2004; Migler et al., 2002). As a result of these complications, the extrapolation of research findings on UV-induced degradation of pure

**Table 1**: Dissociation Energies of Various Bonds (Schnabel, 1981).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Dissociation Energy (kJ/mol)</th>
<th>Corresponding wavelength $\lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O - O</td>
<td>213</td>
<td>562</td>
</tr>
<tr>
<td>C – Cl</td>
<td>326</td>
<td>367</td>
</tr>
<tr>
<td>C – C</td>
<td>351</td>
<td>341</td>
</tr>
<tr>
<td>C – N</td>
<td>330</td>
<td>363</td>
</tr>
<tr>
<td>N – H</td>
<td>339</td>
<td>353</td>
</tr>
<tr>
<td>C – O</td>
<td>372</td>
<td>321</td>
</tr>
<tr>
<td>C – H</td>
<td>393</td>
<td>304</td>
</tr>
<tr>
<td>C = C</td>
<td>502</td>
<td>238</td>
</tr>
<tr>
<td>O - H</td>
<td>426</td>
<td>281</td>
</tr>
</tbody>
</table>
polymer resins to compounded and processed products of the same polymer is often unreliable. UV absorption data and degradation data generated on the actual polymer formulation used in practice, processed in a conventional manner, is most useful for assessment of the potential of photodegradation of that product in application.

Several methods can be used to determine the presence of UV absorbing chromophoric sites, including UV and Fourier transform infrared (FTIR) spectroscopy, among others. These methods rely on the knowledge of the functional groups or compounds that correspond to given absorption bands. In this study, an Optical Spectrum Analyzer (OSA Spectro 320) by Instrument Systems, Germany was used; it is a useful tool that gives spectral analysis emission, transmission and reflection spectra. These spectra carry information that directly infers absorbance of any radiation between 200 nm and 880 nm by samples of different materials. The OSA was used to measure the transmission and reflection of UV radiation by the polyethylene. Absorption of UV by these PE films is discussed. Degradation analysis of conventionally processed PE films, processed by film extrusion, was done using dynamic mechanical analysis with a DMA 2980 from TA Instruments, USA. The DMA was used to analyze the temperature dependence of the mechanical behavior (viscoelasticity) of the films. Viscoelasticity is prominent behavior in polymers (Sperling, 2006) and it means that mechanical properties, like stiffness, are time dependent and, therefore, stress dependent. Change in viscoelasticity, and hence mechanical properties, depict a change in the inner structure of the material.

MATERIALS AND METHODS

Commercial 30 µm thick low density polyethylene films processed by blown film extrusion from two Kenyan companies, PIL and Styroplast Kenya Ltd were used as they were received from the supplier. For the purposes of this study the samples were manufactured without any additives, in a similar manner as those that were in Kenyan market for single short time use-and latter banned by the government.

Emission, transmission and reflection measurements

Samples were cut into 70 x 40 mm sizes for UV transmission and reflection measurements. The UV-irradiation was obtained from UV mercury fluorescent lamps emitting light in the region from 250 to 400 nm. The temperature of the samples during the UV transmission and reflection measurements was maintained at 20°C and the relative humidity was 40%. Emission of the mercury fluorescent lamps and the intensity, transmission and reflection by the films, as a function of wavelength, were measured using an OSA aided by SpecWin software (both from Instrument Systems, Germany).

Sunlight exposure

To investigate degradation due to solar radiation and the environment, fresh untreated samples obtained from the same film as those which optical properties were tested, were exposed to natural conditions at Egerton University for a period of 150 days between May and September, 2011. The samples were clipped on stiff cardboards and elevated from the ground facing upward to the sun that is, inclined at 0° with respect to the horizontal. The cardboards were cut to form a rectangular frame, and the samples loosely clipped at the hollow center portion of the frames, to ensure that the largest portion of the sample was not in contact with the cardboard. Dynamic mechanical analysis was done on smaller samples cut out from the center of the exposed bigger samples on the 70th and 150th days.

Mechanical analysis

Measurements were carried out on the DMA model 2980 using the Tension Film clamp. As an exposure rectangular strips of dimensions 30 x 5 mm were prepared by carefully cutting them out of the parent exposed sample longitudinally along the extrusion direction. For the purpose of analyzing degradation, the storage modulus was chosen. The storage moduli values were determined at a frequency of 2 Hz, amplitude of 50 µm and an oscillating force of 0.01 N. The scan temperatures were from room temperature (25 to 100°C) but the 50 to 100°C range was chosen for analysis. To ensure data quality, calibration of the DMA instrument using standard samples supplied with the instrument preceded any measurement done. Control samples (undegraded) were tested for their storage modulus, loss modulus and loss factor, however, only storage modulus was used in the analysis of the data. These measurements were used as a reference for the subsequent measurements of aged /treated samples.

RESULTS AND DISCUSSION

UV, reflection and transmission

Emission of the employed mercury lamp in the ranges 200 to 300 nm and 300 to 400 nm was determined. This is shown in Figures 1 and 2, respectively. The lamps emitted with a number of peaks as shown in the figures with the highest peaks at 242 nm with an irradiance of 0.0475% W/m² and at 360 nm with an irradiance of 3.8590 W/m². The solar UV reaching the earth's surface is between 290 to 400 nm with a maximum peak of 0.5 W/m²/nm at 375 nm measured at sea level. The units of this solar irradiance is given here as spectral irradiance that is, irradiance per unit wavelength. Comparably, the integrated mercury lamp emission in the range of 300 to 400 nm was approximately 10 times the UV available at the earths surface (> 290 nm). The effects of the mercury lamp irradiation therefore, are expected to be different from that of the sun. This study reports on the UV absorption and effects of the sun on the reduction of the storage modulus. Smaller wavelengths, less than 290 nm, do not penetrate the ozone layer (Ranby and Rabek, 1975). These smaller wavelengths are energetic enough to cause direct photolysis when incident on a polymeric material. Radiation above 290 nm is responsible for initiation of peroxidation of the polymer (Dilara and Briassoulis, 2000). As a result natural polymer degradation follows the peroxidation route rather than
direct photolysis.

As shown in Figure 3 the reflection of the UV radiation by the 30 µm PE film within the range (200-300) nm was generally below 20%, except at 274, 208, 232 and 292 nm with highest peaks of 70 and 100% at 274 and 292 nm respectively. These percentages for the reflection and transmission are read in reference to the 100% reflection and transmission reference lines respectively, e.g. light reflection of 20% is read as 120% from the spectral graph. This low reflection suggests that most of the radiation actually entered the material film either for absorption or transmission. Reflection of the UV radiation by the 30 µm PE film within the range 300 to 400 nm is shown in Figure 4. Reflection peaked at 311, 314, 358 and at 375 nm.

In the (200-300) nm range transmission was lower than 20% except at 243, 228 and 237 nm where transmission was above 30%, peaking at 243 nm with above 80% as shown in Figure 5.

Given that the reflection in this range 200 to 300 nm as
shown in Figure 3 was generally low, it suggests that the samples absorbed this UV. The transmission spectrum shown in Figure 6 has absorption of less than 20% in the (300 to 325) nm, (328 to 360) nm and (378 to 394) nm ranges except at 349 and 359 nm with slightly above 20%. There also existed transmission peaks at 327 nm, five between 358 and 376) nm, the highest at 363 nm with transmission of almost 80% and a single line near 397 nm. It also shows a transmission of less than 20% of wavelengths between 330 and 345 nm. This could be the
emission spectra or fluorescence spectra of LDPE which is normally at 330 to 345 nm (Konar and Ghosh, 1989; Teyssedre et al., 2005). There was no emission of UV between 300 and 310 nm as shown in Figure 2 (except at 306 nm of 20%) and hence the same wavelengths show missing reflection and transmission in Figures 4 and 6 respectively. The low reflectivity within the 318 to 358 nm region in Figure 4 where the transmission was also lower than 20%, except at 326 nm, as shown in Figure 6 suggests that the radiation was absorbed. This absorption may correspond to the excitation spectra of LDPE (Konar and Ghosh, 1989).

Figure 5. UV Transmission within 200 to 300 nm range.

Figure 6. UV Transmission of 30 microns sample at the range 300 to 400 nm
UV absorption

Using the simple formula, \( A = 1 - (T + R) \) where \( A \) = percentage absorption, \( T \) = percentage transmission and \( R \) = percentage reflection of the incident UV and in Excel program, the UV absorption spectra were obtained as a percentage of incident UV. Figures 7 and 8 shows the absorption percentages in the ranges (200 to 300) nm and (300 to 400) nm respectively, in reference to the 100% line. Absorption was generally low, especially at
Table 2. UV absorption of 30% and above

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Absorption %</th>
<th>Wavelength (nm)</th>
<th>Absorption %</th>
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</thead>
<tbody>
<tr>
<td>317</td>
<td>30</td>
<td>222</td>
<td>41</td>
</tr>
<tr>
<td>282</td>
<td>32</td>
<td>298</td>
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<td>249</td>
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<td>300</td>
<td>33</td>
<td>223</td>
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<td>360</td>
<td>40</td>
<td>354</td>
<td>62</td>
</tr>
<tr>
<td>211</td>
<td>41</td>
<td>392</td>
<td>62</td>
</tr>
</tbody>
</table>

Figure 9. DMA plot of 30 µm PE sample, showing storage and loss modulus and damping factor. The values of the storage and loss modulus and shape of the damping factor curve as expected suggests that the sample measurements are made at the rubbery plateau of the polymeric material.

Low wavelengths, with absorption peak values above 30% shown in Table 2. These low wavelengths (below 300 nm) were given low attention since degradation of polyethylene is known to be caused by absorption of UV by various internal or external impurities, usually photo-absorbing chromophores rather than direct photolysis. These chromophores absorb UV at or above 290 nm (Gijsman and Dozeman, 1996). Many wavelengths that had absorption above 30% were in the range (300 to 400) nm. Normally, the chain scission quantum efficiency of solid polymers is low (Nguyen et al., 2002), meaning that for substantive degradative process to be initiated, the presence of a high number of incident photons is needed.

Dynamic mechanical analysis

Figure 9 shows the storage modulus, loss modulus and loss factor taken before any treatment. Samples from both companies showed no difference in their properties. For the special case of unconstrained uniaxial tension, the stiffness $k$ of a sample is given by:

$$k = \frac{AE}{L}$$

Where $A$ - Cross sectional area, $E$ - Modulus, $L$ - Length of the sample. The slow drop of modulus confirms that the polymer is within the rubbery plateau. Figure 10 shows
Figure 10. Reduction of storage modulus of a 30 μm PE film at 0 days (control) and after 70 and 150 days exposure to natural environment in Egerton University, Njoro.

Figure 11. Decrease in storage modulus, with a hypothetical fitted trend.

the change of storage modulus as the films were exposed to sunlight for 75 and 150 days. Before any treatment the storage modulus measured is shown in Figure 10 as the control, after 70 and 150 days the storage modulus curves measured had the same gradient but displaced downwards indicating that exposure to sunlight led to drop in storage modulus. The storage modulus is proportional to the peak energy stored per cycle in the sample; hence a measure of its viscoelasticity. Chain breakages (degradation) are associated with a decrease in energy storage capacity during a strain and this is recorded in a decrease of storage modulus (Choon et al., 2004). This loss of storage modulus and hence viscosity of a material, makes the material brittle with subsequent breakage on application of external force (Xie and Huilin, 2007). Studies done earlier shows that the action of sunlight on LDPE films begins with photo-oxidation of the outer layers, which after direct contact with atmospheric oxygen this oxidation can proceed rapidly through radical chain oxidation reactions. The inner layers which cannot be reached by atmospheric oxygen degrade slowly through photo-reactions of peroxy radicals. In addition this photodegradation is known to start at the amorphous region of the polymeric material (Dilara and Briassoulis, 2000).

The drop of storage modulus averaged for the range (50 to 98°C), fits a hypothetical polynomial of order two fairly well as shown in Figure 11. This implies that the polymer take much time to degrade to low modulus values. Our results are consistent with other studies that
CONCLUSION AND RECOMMENDATIONS

The UV absorption by the PE films used in this study was below 62% except at 216 nm where absorption is 89%. This suggests existence of a concentration of chromophoric sites such as C=C, C=O and C-O bonds which are known to absorb within these wavelengths ranges and initiates photo-degradation. Other concentrations possible could be hydroxyls, carbonyl, carboxyl, ketonic compounds or amino groups as chromophores and catalyst residues containing Ti, Al and Cl (Gijssman et al., 1999). These initiators of photo-degradation can be introduced to the polymer during manufacture (that is, polymerization) and during processing (that is, extrusion). As expected therefore, these PE films were relatively unstable to sunlight as shown by the reduction of the storage modulus, but the degradation is slow as compared to biodegradation. For applications in horticulture (e.g. for green houses), use of stabilizers e.g. UV absorbers, Ni quenchers and hindered amine light stabilizers (HALS), as it has been done (Khan and Hamid, 1995; Gijssman and Dozeman, 1996; Dilara and Briassoulis, 2000), is encouraged. For short term consumers e.g. food packaging, fast degradation can be encouraged by addition of chromophores capable of near visible radiation absorption. In other words, different degrees of degradation in the PE can be induced depending on the use of the material, expected route of disposal and possibility of re-use. This absorption should however be able to ignite degradation and quick fragmentation of these products that ends in landfills. This could be one way of reducing pollution menace created by the high use of PE for short-term uses in places where collection for recycling is not possible.

Conflict of Interest

The authors have not declared any conflict of interest.

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