The Effect of Ultraviolet and Ultraviolet - Ozone Exposure on Polymers

Marlene Lawston
Niskayuna High School
1626 Balltown Rd, Niskayuna, NY 12309

Abstract

Ultraviolet (UV) degradation is a common result of the exposure of polymers to ultraviolet rays and is a challenging problem to material engineers. Different types of polymers have unique structures making some polymers more susceptible to UV attack and others more UV-stable. By using Fourier Transform Infrared Spectroscopy to compare five different polymer samples, polyethylene (with adhesive) was determined to be the least UV-stable while Polyimide was determined to be the most UV-stable. Further research to be conducted should include testing the UV-stability of multiple types of polyimides and more stages of UV-Ozone exposure.

Introduction

- UV degradation is often the result of exposure of polymers to ultraviolet rays and has been a challenging problem to material engineers because autoxidation reactions that occur as the product is exposed to UV rays have immediate impacts on properties that determine the service life of the product.
- Some results of UV degradation are discoloration, viscosity changes, char formation, cracking and loss of adhesion (figure 1.1).
- Many synthetic polymers are not UV-stable and are susceptible to cracking and discoloration as a result of exposure to UV rays.
- This degradation is often a result of the ultraviolet rays interacting with the tertiary or aromatic carbons to form free radicals which then react with oxygen in the atmosphere to form carbonyl groups in the main chain of the polymer. This process can be seen in figures 1. and 1.2.
- Certain polymers are more UV-stable than others; fourier transform infrared spectroscopy (FTIR) allows this stability to be tested.
- **Hypothesis:** What is the effect of UV-rays and UV-ozone rays on different types of plastic polymers?
• As the polymers are exposed to UV rays, oxidation will occur. The longer they are exposed, the more the oxidation reaction will occur and cause carbonyl groups to form. Evidence of this formation can be observed using Fourier transform infrared spectroscopy. A C=O peak at around 1700 cm$^{-1}$ would indicate that this process occurred and that carbonyl groups are present.

![Figure 1. Diagram of Reaction due to ultraviolet radiation exposure.](image)

**Figure 1.** Diagram of Reaction due to ultraviolet radiation exposure.

![Figure 1.1 On left: rope after exposure to UV rays. On right: Rope before exposure to UV rays.](image)

**Figure 1.1** On left: rope after exposure to UV rays. On right: Rope before exposure to UV rays.

![Figure 1.2 Degradation process of polymers.](image)

**Figure 1.2** Degradation process of polymers.

### 2.1 Experiments

DSC was used to confirm the identity of various polymers and FTIR was used to show the effect of exposing the plastic film polymer samples to ultraviolet rays and to ozone. Four different IR spectrums were taken for each sample: one before exposure to any ultraviolet rays, one after exposure to ultraviolet rays for thirty minutes, one after exposure to ultraviolet rays and for ten minutes and one after exposure to ultraviolet-ozone rays for an hour. After the data was obtained, the UV-stability of each sample was compared to the others.
2.2 Samples

The polymer films used in the experiment are shown in figure 2.

(a) (b) (c)

(d) (e)

Figure 2. Pictures of the polymer film samples used in the study. (a) Glad with adhesive, (b) Polyimide film, (c) Popcorn bag package, (d) Walmart grocery bag, (e) Bag (“LDPE sign on it”).

2.3 Differential Scanning Calorimetry

DSC is a thermal analysis instrument that measures glass transition, melting, and crystallization temperatures during the heating and cooling scans of polymers. In this experiment, the polymers that made up samples (a) through (e) were identified by their packaging; however, DSC was used to confirm their identities. On the DSC graph for each sample, the peak temperature of melting was labeled for comparison since each polymer has a different melting point.

TA Instruments DSC (Model Q2000) was used with aluminum sample pans, and sample weight for analysis typically ranges between 2 mg and 3 mg. Samples were heated/cooling at a rate of 20 oC/min for sample (a) and 10 oC/min for samples (b)-(f). TA Universal Analysis 2000 software was used to label the peak temperature of melting for comparison. Table 1 shows the melting point ranges for the identified polymers.

Table 1. \(T_m\) for each sample (melting point)

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>(T_m) (Celsius)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liner Low Density Polyethylene</td>
<td>110</td>
</tr>
<tr>
<td>Polyimide</td>
<td>------</td>
</tr>
<tr>
<td>Glass Transition (240-250)</td>
<td></td>
</tr>
<tr>
<td>Polypropylene</td>
<td>160</td>
</tr>
<tr>
<td>High Density Polyethylene</td>
<td>130</td>
</tr>
</tbody>
</table>
Sample A (Liner Low Density Polyethylene-High Density-like)
Experimental melting point- 128.28 degrees Celsius
Accepted melting point-130 degrees Celsius
The identity of the polymer matches the product label.

Sample B (Polyimide)
Experimental melting point-No melting, Glass transition around 238.88 degrees Celsius
Accepted Glass transition Range- 240-250 degrees Celsius
Identity of polymer matches the label.
Sample C (Polypropylene)
Experimental melting point- 159.34 degrees Celsius
Accepted melting point- 160 degrees Celsius
Identity of polymer matches product label

Sample D (Liner Low Density Polyethylene-High Density-like)
Experimental melting point- 126.74 degrees Celsius
Accepted melting point-130 degrees Celsius
The identity of the polymer matches the product label.
Sample E (Linear Low Density Polyethylene-Low Density-like)

Experimental melting point- 121.78 degrees Celsius

Accepted melting point- 110 degrees Celsius

The identity of the polymer matches the label however, it looks like there is an additive to this sample.

The DSC graphs show that the materials being tested all have different thermal properties and that they match the identity of the product label.

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a chemical analysis technique based on the absorption of infrared light by molecules which produces a unique spectrum for each type of molecule. FTIR can help identify materials, determine the quality or consistency of a sample and determine the amount of components in a mixture. An infrared spectrum of a molecule shows absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. Because each molecule is a different combination of atoms, no two compounds produce the exact same infrared spectrum. Figure 3 shows IR frequencies for various functional groups.
It is important to note that on infrared spectra C=O stretching occurs in the wave number region $1670-1820 \text{ cm}^{-1}$ and C-H stretching occurs around $3000 \text{ cm}^{-1}$. When present, these peaks are particularly distinct.

A Perkin-Elmer (Model Spectrum Two) machine was used for taking FTIR spectra in the wavelength range of $4000$ to $700 \text{ cm}^{-1}$. FTIR samples were prepared by taping polymer film samples on a paper business card with a circular aperture of about three cm in diameter.

**Figure 3.** It is important to note that on infrared spectra C=O stretching occurs in the wave number region $1670-1820 \text{ cm}^{-1}$ and C-H stretching occurs around $3000 \text{ cm}^{-1}$. When present, these peaks are particularly distinct.

**3. Results and Discussion**

After IR spectra were taken from each original sample, the samples were exposed to UV rays for thirty minutes. When IR spectra were obtained from the samples that were exposed to UV rays for thirty minutes, most did not display noticeable change. This could be due to the sensitivity of the FTIR machine or the fair UV-stability of each sample.
Furthermore, we exposed the samples to 10 minutes of UV rays and ozone and then to a full hour of UV rays and ozone. The ozonized samples generally displayed more evidence of chemical change; this is expected since the presence of ozone accelerates the oxidation process. An IR of sample (b) after a full hour of exposure to UV-Ozone was not obtained due to technology malfunctions. Table 2 summarizes when each polymer’s IR spectrum was observed to display a change. The resulting IR spectra for each sample are pictured and discussed below.

**Table 2. Summary of polymer types and observations from FTIR**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Type(s) of Polymers</th>
<th>Polymer Structure</th>
<th>Change after UV exposure for 30 minutes</th>
<th>Change after UV-Ozone exposure for 10 minutes</th>
<th>Change after UV-Ozone for 1 hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>LLDPE-HDPE-like</td>
<td><img src="image" alt="LLDPE-HDPE-like" /></td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>(b)</td>
<td>PI</td>
<td><img src="image" alt="PI" /></td>
<td>No</td>
<td>No</td>
<td>N/A</td>
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<tr>
<td>(c)</td>
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<td><img src="image" alt="PP" /></td>
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<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>(d)</td>
<td>LLDPE-HDPE-like</td>
<td><img src="image" alt="LLDPE-HDPE-like" /></td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>(e)</td>
<td>LLDPE-LDPE-like</td>
<td><img src="image" alt="LLDPE-LDPE-like" /></td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Sample A

IR Spectra of Sample A for Each Stage of Exposure to UV-rays and to UV-rays with Ozone

Figure 5. IR spectra of sample (a), Linear Low Density Polyethylene

This sample was the only one from the study to show evidence of oxidation as a result of exposure to solely UV rays after 30 minutes (Table 1). This is likely due to the adhesive layer on the sample which is subject to oxidation. As the sample was exposed to UV and UV-Ozone, the peak around 1700 cm\(^{-1}\) formed and became more distinct as the stages of exposure increased (Figure 5). The peak at 1700 cm\(^{-1}\) is a result of C=O stretching and is due to the oxidation reaction that formed the carbonyl group. At 3500 cm\(^{-1}\) a second bump appeared. This could be water absorbed by the sample since the polymer

\[\text{Absorbance} \]
\[\text{Wavenumbers/cm}^{-1}\]

Fig. 6. Changes in the spectra of the PVA hydroxyl stretching vibration with the water content in the membrane: a: 4.2%, b: 6.3%, c: 10.2%, d: 19%, e: 40%, f: 59% (the spectra were obtained by subtracting the spectra of swelling membranes from that of the dry ones).
became polar after oxidation. IR spectra of hydrophilic polymers at lower water absorbance percentages show a similar bump [1] (Figure 6).

It is evident that sample (a) has poor UV-stability and appears to be the least stable of all the samples tested. It makes sense that this would not be UV-stable because it was designed to preserve food that would most likely be stored in cold environments away from ultraviolet rays such as a refrigerator. In addition, the early oxidation may have occurred on the adhesive and not within the polymer itself.

**Sample B**

![FTIR Sample B For Each Stage of Exposure to UV-rays and UV-rays with Ozone](image)

**Figure 7.** IR spectra of sample (b), polyimide.

Sample (b) was the only sample that did not change after it was exposed to UV and UV-Ozone and although an IR was not taken for the example after an hour of UV-Ozone exposure, polyimides are known to have excellent UV-stability [3] so there probably would not have been detectable change. NASA has even used polyimides on its deep space telescopes such as Hubble because of their UV-stability [3]. In addition, the United States Space Program uses a material made from polyimide film called Kapton® for applications such as the solar array and thermal management both of which require UV-stable materials [2]. The IR spectra in Figure 7 show that as the sample was exposed to UV and UV-Ozone, no significant peaks appeared. This indicates that the polymer was not oxidized like the others and is therefore very UV-stable.
Sample C

FTIR of Sample C Before and after One Hour of UV-Ozone Exposure

Figure 8. Sample (c) Polypropylene before and after one hour of UV-Ozone exposure. No change was observed after thirty minutes of UV and after 10 minutes of UV-Ozone, to make the graph more legible, they were not included.

Sample D

IR Spectra of Sample D for Each Stage of Exposure to UV and UV with Ozone

Figure 9. Sample (d) Liner Low Density Polyethylene (High Density Polyethylene-like)
Sample (c) did not show signs of being affected by the UV or UV-Ozone until the last stage when it was exposed to UV-Ozone for a full hour and a C=O peak formed (Figure 8). Compared to sample (a) (the adhesive plastic wrap made from liner low density polyethylene), sample (c) is more UV-stable.

This sample is interesting because before it was exposed to UV-rays it already contained a small peak at 1700 cm\(^{-1}\). This indicates that a type of chemical (most likely a dye) with C=O bonds was present. It is similar to polypropylene in that no change in its IR spectrum was detected until it was exposed to UV-Ozone for an hour.

**Sample E**

**Figure 10.** Sample (e) Liner Low Density Polyethylene (Low Density Polyethylene Like) IR with distinct peak at 1700 cm\(^{-1}\) after exposure to UV-rays and Ozone for one hour.

Samples (d) and (e) were both made of LLDPE, however, sample (d) was more HDPE-like. The IR spectra of Sample (d) were more saturated than the spectra of (e). This is likely because sample (d) was from a Walmart bag which was opaque but sample (e) was from a transparent plastic bag. C=O stretching in both samples was not observed until they were exposed to UV-rays and Ozone for an hour.

**Conclusion**

It is evident that when polymers are exposed to UV rays and ozone, a carbonyl peak appears in the 1700 cm\(^{-1}\) region. This is a result of the formation of C=O containing groups (such as carboxyl, ketone or aldehyde groups) from the oxidation chain reactions that occur on the polymer chains after the polymer is exposed to UV rays and ozone. Most polymers are susceptible to UV attack.
because they contain tertiary carbons or aromatic carbons. Notable exceptions are the polyimide polymers which contain nitrogen atoms in their structure, increasing their UV-stability. The results show that the polyethylene with adhesive was the least UV-stable since it was the first to display evidence of an oxidation reaction which was the C=O peak at 1700 cm\(^{-1}\) (after 30 minutes of UV exposure). This poor UV-stability can be contributed to the adhesive. Most of the early oxidation that showed on the FTIR could have occurred on the adhesive itself rather than directly on the polymer. It can be concluded that polyimide is the most UV-stable from the IR spectra of the polymer which showed no change when exposed to UV rays or ozone and from other studies conducted by Dupont. Future experimentation should include one hour exposure of polyimide to UV-rays and ozone for better data comparison, more stages of UV-ozone exposure and DSC analysis of each polymer after every stage of UV-ozone exposure.

**Acknowledgement**

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**References**


