

Shedding Light on Marine Pollution

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Abstract

Massive amounts of plastic waste have been accumulating in the Great Pacific Garbage Gyre and are posing a threat to the marine environment. Since little is known about the degradation of plastics in this marine setting, we adopt the goal of modeling the photodegradation of a common plastic, polyethylene, in seawater. Plastic in the ocean is exposed to ultraviolet (UV) light from the sun, which causes photodegradation, a natural source of plastic decomposition.

We develop two models to describe the rate of photodegradation of polyethylene floating in seawater, a Low-Transmittance of Light Model (LTM) and a High-Transmittance of Light Model (HTM). Using the constant rate of UV irradiance and the average bond dissociation energy of carbon-carbon single bonds (C–C), we calculate the mass lost per unit of time.

The results from our models are realistic. The HTM predicts that a rectangular prism of polyethylene $1 \times 1 \times 2$ cm weighing 1.87 g will lose 1.27 g of mass in one year; the LTM predicts that a hollow sphere with thickness 0.0315 cm, radius 5 cm, and weight 9.145 g, partially submerged in low-transmittance water, will lose 0.190 g of mass in the first year. The design of our models allows us to model other shapes, adjust the intensity of UV light, and realistically predict the photodegradation of polyethylene.

Introduction

The accumulation of plastic debris in our oceans is quickly coming to light as one of the most prevalent and devastating threats to the marine environment. The “Great Pacific Ocean Garbage Patch” is one of many areas of wind-current convergence where massive amounts of debris collect and stew. The “garbage” is not primarily in the form of bottles and bags,

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but rather as tiny particles referred to as *neustonic plastics*. These neustonic plastics are the products of degradation of post-consumer and industrial wastes and may pose great risk for marine life. The nature of the degradation of plastics has thus become an important element in the study of this environmental catastrophe.

We focus specifically on the photolytic degradation of polyethylene plastic accumulating in the gyre. We consider

- the UV radiation reaching the surface of the ocean;
- the energy required to break the bonds in polyethylene; and
- physical considerations concerning buoyancy, mass, and surface area of the plastic particles.

Description of the Problem

We consider the degradation of floating polyethylene fragments by photolytic degradation. The fragments are considered to be hollow spheres partially filled with seawater, to represent common post-consumer waste containers. The fragments are partially submerged in water with either low or high transmittance of light. High-transmittance water can use the entire effective surface area of the fragment to model degradation, while for fragments in low-transmittance water only the portion of the fragment above water will be susceptible to photolytic degradation [Ivanhoff, Jerlov, and Waterman 1961].

Ultraviolet light is assumed to hit the fragment orthogonally to the plane of the ocean, thereby exposing a two-dimensional surface area of effective area c . We relate c to the radius r of the fragment; the mass m of the fragment depends on both. The goal is to model these relationships over time to describe the loss of mass experienced by a polyethylene fragment.

Photolytic Degradation of Polyethylene

Polyethylene is a polymer consisting of long chains of the monomer ethylene [Carey and Sundberg 2007]. There are two types of bonds present in polyethylene: carbon-carbon single bonds (C–C) and carbon-hydrogen single bonds (C–H) [Leeming 1973]. Polyethylene has the structure



where n is the number of monomers in the chain.

Photodegradation is a process by which chemical bonds are broken when struck by light [Carey and Sundberg 2007; Okabe 1978]. The light must carry enough energy to cleave a bond, which can be estimated using

the average bond dissociation energy [Leeming 1973]. The equation

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

where h is Planck's constant and c is the speed of light, can be used to find the minimum wavelength λ of light that carries enough energy to break the bond [Skoog, Holler, and Crouch 2007]. For example, the energy to cleave a C–C single bond is $5.778 \times 10^{-19} \text{ kg} \cdot \text{m}^2/\text{s}^2$. Using $h = 6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}$ and $c = 3 \times 10^8 \text{ m/s}$, we find $\lambda = 344 \text{ nm}$, a wavelength in the ultraviolet.

Thus, when polyethylene is exposed to ultraviolet light (UV) with a wavelength of 344 nm, C–C single bonds are cleaved and free radicals are formed that react quickly with O_2 to form peroxy radicals. Then either the peroxy radicals continue a chain reaction of radical formation or else two free radicals react to terminate the chain reaction [Carey and Sundberg 2007; McNaught and Wilkinson 2007; Trozzolo and Winslow 1967]. The pathway of free radical chain reactions and termination reactions can be seen in Figure 1.

Photo oxidative reaction mechanism:

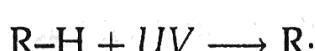


Photo oxidation termination reactions:

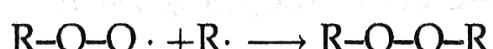


Figure 1. Reactions of peroxy radicals.

The cleavage of C–C single bonds breaks the polyethylene into fragments and the polyethylene loses mass. The rate of degradation can be estimated by assuming that every time a C–C bond is cleaved by UV light, a monomer is removed from the original mass of polyethylene. The rate at which the C–C bonds can be cleaved depends on the amount of UV light emitted by the sun, which is $0.0005 \text{ watts/m}^2 = \text{J/s} \cdot \text{m}^2$ [Karam 2005]. Since the energy to break a C–C bond is $5.778 \times 10^{-19} \text{ J}$ and there are Avogadro's number (6.022×10^{23}) molecules in a mole, we can find via unit conversion the rate of photodegradation of polyethylene:

$$\begin{aligned}
 \frac{1 \text{ C-C bond}}{5.778 \times 10^{-19} \text{ J}} &\times \frac{0.0005 \text{ J}}{1 \text{ s} \cdot 1 \text{ cm}^2} \times \frac{1 \text{ mole polyethylene}}{6.022 \times 10^{23} \text{ C-C bonds}} \\
 &\times \frac{28 \text{ g monomer polyethylene}}{1 \text{ mole polyethylene}} \\
 &= \frac{4.02 \times 10^{-8} \text{ g monomer polyethylene}}{\text{s} \cdot \text{cm}^2}
 \end{aligned}$$

General Assumptions

- Since mechanical degradation due to torque on plastic is minimal due to the small size of plastic particles [Tipler 2004], and colliding plastic particles are rare due to low particle density [Moore, Lattin, and Zellers 2005], in our model we neglect mechanical degradation.
- Polyethylene particles float in seawater, since medium-density polyethylene's density is 0.937 g/ml [Chevron Phillips Chemical Company n.d.] and average density of 35 ppt saline seawater at 15°C is 1.0255 g/ml. We neglect water currents.
- The source of UV light is a constant average at sea level in the Pacific Northwest [Karam 2005].
- Polyethylene in the model does not contain UV stabilizers and is medium density.
- Polyethylene is composed of ethylene monomers and the average bond dissociation energy for C-C single bonds is used to predict the energy needed to cleave the C-C bonds [Leeming 1973].
- Only the portions of the plastic fragments that are perpendicular to the UV light are subject to photolytic degradation.
- Only the effective surface area above water can receive UV light.
- The photolytic cleavage of C-C bond in the model is a fast forward reaction ($K_{rxn} \gg 1$) and the reverse reaction is very slow. Immediately after the bond is cleaved, the free radical forms and is quenched by any of the termination reactions that also have a $K_{rxnb} \gg 1$. We also assumed 100% quantum efficiency of these reactions.

High-Transmittance Model

This model considers the degradation of a square prism of polyethylene on a flat surface on land or in water with a very high transmittance of light. One of the faces of the prism faces directly perpendicular to the UV

light source. Let K_1 the rate of degradation from the calculation on p. 168, 4.02×10^{-8} (g monomer polyethylene)/s·cm². Then

$$\int_0^y \int_0^x \int_0^t K_1 dt dx dy = K_1 txy,$$

due to the simple geometry. The result is a simple linear model of degradation based on time and area.

Consider a square prism with the dimensions of 1 cm × 1 cm × 2 cm, with an area 1 cm × 1 cm exposed to UV radiation. It has an initial mass of 1.87 g [Chevron Phillips Chemical Company n.d.]. After one year of UV exposure, about two-thirds—1.27 g of polyethylene—is lost as a result of photolytic degradation.

Low-Transmittance Model

A primary factor in describing the amount of UV light that a fragment of plastic absorbs is the effective surface area perpendicular to direct sunlight. Since the North Pacific Gyre is a collection of floating debris, we use Archimedes' principle to relate the buoyancy of a piece of plastic to its effective surface area. For simplicity, we neglect the effect of air in the container on buoyancy. Archimedes' principle states that "the buoyant force on a submerged object is equal to the weight of the fluid that is displaced by that object" [Hodanbosi 1996]. In addition, since the plastic is in kinetic equilibrium in the vertical direction, its buoyant force must be equal in magnitude to its weight:

$$F_{\text{buoyant}} = W_{\text{plastic}} = M_{\text{plastic}} g = M_{\text{water displaced}} g = V_{\text{plastic submerged}} d_{\text{water}} g,$$

where M is mass, W is weight, V is volume, d is density, and g is acceleration due to gravity. Thus, we have

$$M_{\text{plastic}} = V_{\text{plastic submerged}} d_{\text{water}},$$

whose right-hand side can be calculated from the triple integral

$$\int_x^\pi \int_0^{2\pi} \int_{r-h}^r d \cdot \rho^2 \sin \phi d\rho d\theta d\phi,$$

where h is the thickness of the plastic and x is the angle from the zenith to the point on the sphere's surface where the sphere contacts the water level (see **Figure 2**). Setting this integral equal to the total mass of the plastic, we can find x . Trigonometry relates the radius r of the sphere and the angle x to the effective surface area c of the sphere exposed perpendicularly to UV rays, as indicated in **Figure 2**.

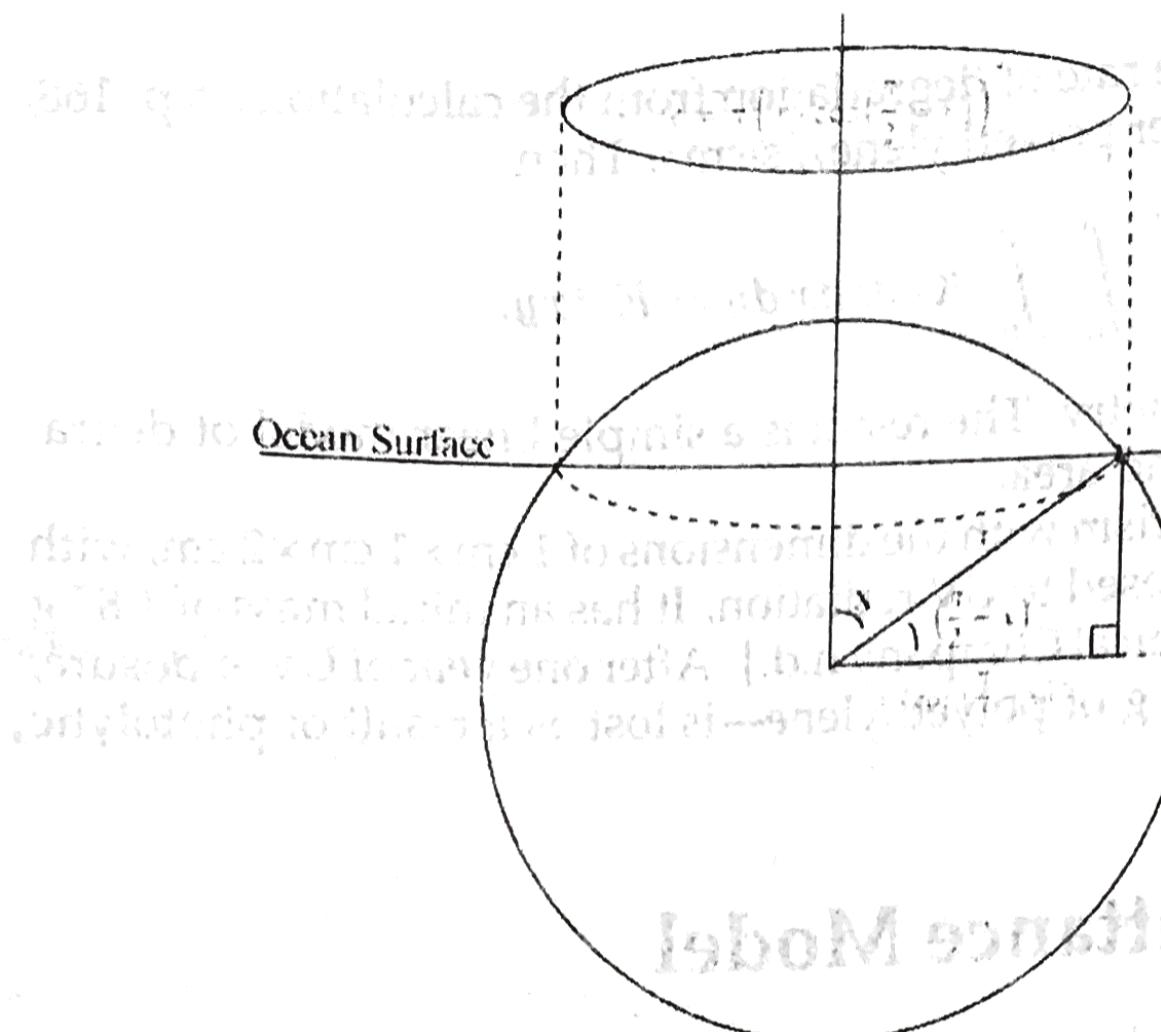


Figure 2. Geometry of a sphere at the ocean's surface.

As shown in **Figure 2**, the effective solar radius is

$$r_e = r \cos\left(\frac{\pi}{2} - x\right).$$

By subtracting the volumes of two concentric spheres with $\Delta r = h$, then multiplying by the density l of the plastic, we get

$$M = \left[\left(\frac{4}{3} \pi r^3 \right) - \left(\frac{4}{3} \pi (r-h)^3 \right) \right] l.$$

We solve for r :

$$\pi h^2 \pm \sqrt{\pi^2 h^4 - \pi h \left(\frac{4}{3} \pi h^3 - \frac{m}{l} \right)} \\ r = \frac{-\pi h^2 \pm \sqrt{\pi^2 h^4 - \pi h \left(\frac{4}{3} \pi h^3 - \frac{m}{l} \right)}}{2\pi h}$$

We define a constant C based on the relationship between the mass (in grams) of plastic and the total bond energies (in joules) within that mass, based on the molar mass and the average bond energy of polyethylene:

$$C \equiv 1 \text{ J} \times \frac{1 \text{ mole}}{348000 \text{ J}} \times \frac{28 \text{ g}}{1 \text{ mole}} = 8.046 \times 10^{-5} \text{ g/J.}$$

Ultraviolet light is the source of energy in this model. A true empirical value for the amount U ($\text{J/cm}^2 \cdot \text{yr}$) would need to be measured on site. The

product UC has units of $\text{g}/\text{cm}^2 \cdot \text{yr}$. To solve for a total change in grams over a specific time and area, we integrate the term with respect to time and then with respect to area:

$$\int_0^t \int_0^{2\pi} \int_0^{r_e} UC \cdot r dr d\theta dt = \Delta m = UCr_e^2\pi t.$$

Subtracting from the initial mass, we have

$$M_{\text{final}} = m - UVCr_e^2\pi t.$$

Using the Low-Transmittance Model, consider a hollow sphere with thickness 0.0315 cm, radius 5.00 cm, and initial mass 9.145 g. After one year of UV exposure, the loss in mass is 0.190 g of polyethylene. The rate of degradation can be visualized in **Figure 3**.

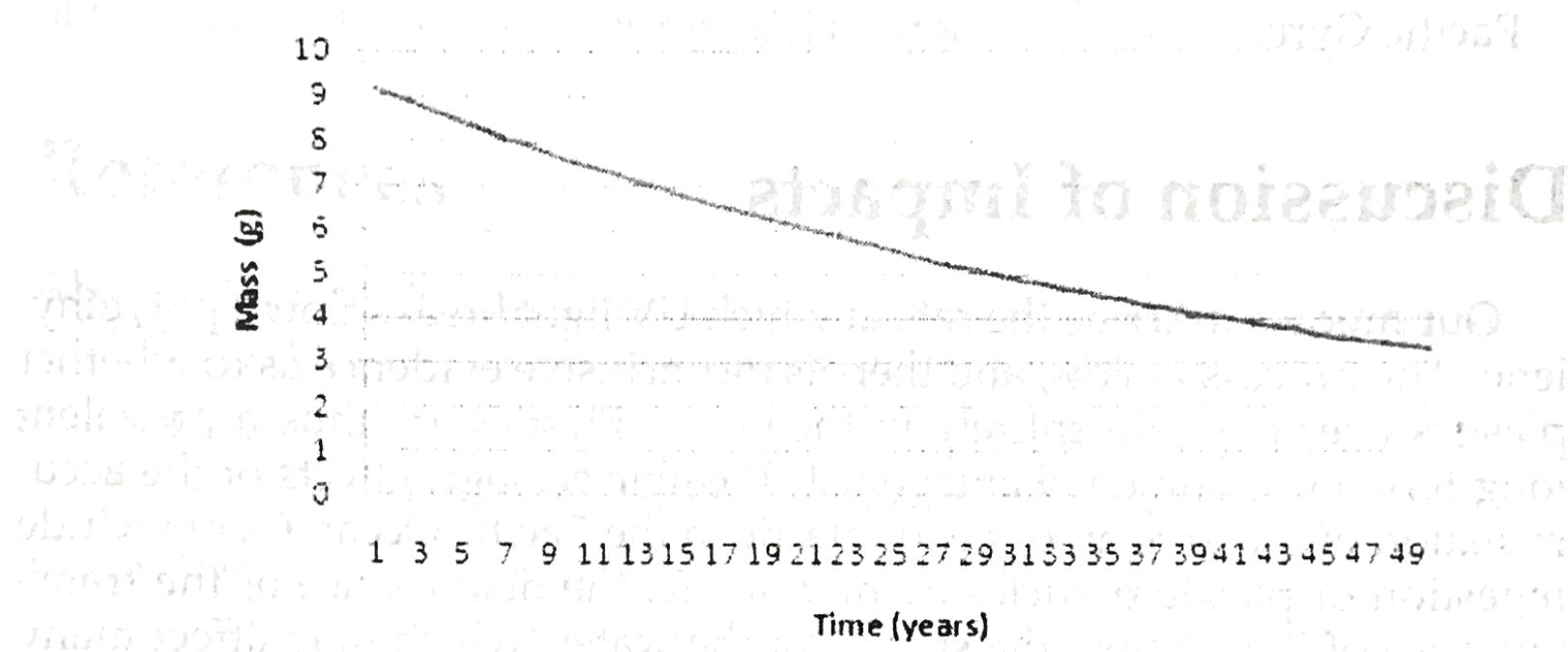


Figure 3. Degradation of mass of polyethylene sphere over time.

Comparisons and Limitations

We develop two models to determine mass lost to photodegradation from a piece of polyethylene plastic exposed to UV light. The High-Transmittance Model models the polyethylene as a rectangular prism; the Low-Transmittance Model models the exposed effective surface area of a hollow sphere of a particular thickness, partially submerged. Depending on the conditions of the water (density and transmittance) and the shape of the object, the models can be modified to describe photodegradation of polyethylene in many other shapes in high- or low-transmittance water.

To increase the accuracy of our models, a few main points need additional research and refinement:

- The value U used for irradiance of UV light in the North Pacific Ocean needs to be verified.
- Mechanical degradation will also take place and should be included.
- The models do not describe the fact that particles tend to converge on a similar size around 3–5 mm [Yamashita and Tanimura 2007].
- Many polyethylene products contain UV stabilizers that increase the longevity of the plastic by inhibiting the free-radical chain reaction [Carey and Sundberg 2007].
- Polyethylene can vary in density. Our model uses medium-density polyethylene (MDPE).
- Plastics are not just on the ocean surface but also at depths up to 100 ft.
- Polyethylene, although very common, is not the only plastic in the North Pacific Gyre.

Discussion of Impacts

Our models describe the rate at which UV light breaks down polyethylene. The process is slow, and there is inconclusive evidence as to whether plastics ever degrade entirely in the Gyre. Plastics are thus a prevalent long-term environmental antagonist. Possible ecologic effects of the accumulation of massive amounts of plastic in the Pacific Ocean Gyre include ingestion of plastic particles by marine life, the disturbance of the transmittance of light below the surface of the water (which may affect many organisms' ability to synthesize energy from photosynthesis), and the distribution of hydrophobic pollutants. Our model relates to the ingestion of plastic particles by marine life because it predicts the mass of fragments at a given time and marine organisms may confuse plastic fragments that are similar in size to their normal food source.

Contributing to the growing problem of plastic pollution in the ocean is the lack of governmental regulation on pollution by cruise ships. During a one-week trip, a typical cruise ship produces 50 tons of garbage. Regulations are tricky though, because international waters do not have well-defined environmental authority structures, and monitoring is minimal [State Environmental Resource Center 2010]. Stronger regulations and monitoring systems are required to decrease the impact of pollution by cruise ships.

Land-based sources contribute up to 80% of marine debris, 65% of which is from post-consumer plastics that were improperly disposed of [Algalita Marine Research Foundation 2009]. This means that the plastics are littered, not just that they are not recycled. Many states have laws against

littering, but monitoring efforts need to be improved. Education and monitoring programs may be expensive, but the cost would likely be small when compared to the potential for environmental protection.

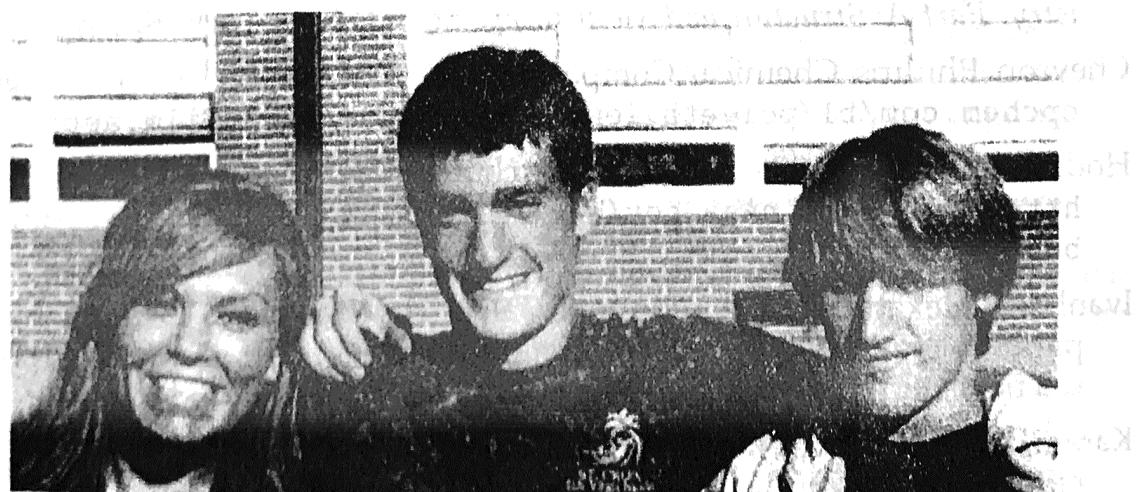
Conclusion

We propose two realistic models for the photodegradation of polyethylene. The first model is for a solid chunk of polyethylene either on land or in water with 100% transmittance of light. The second model is more complex and considers a partially submerged hollow sphere of polyethylene that is degraded only over the effective surface area. Our models can accurately describe degradation of partially degraded or intact plastic products, since the initial physical properties (size, mass, etc.) of polyethylene can be varied in both models. The ease of customization and thorough consideration of realistic variables make our models suitable for use.

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