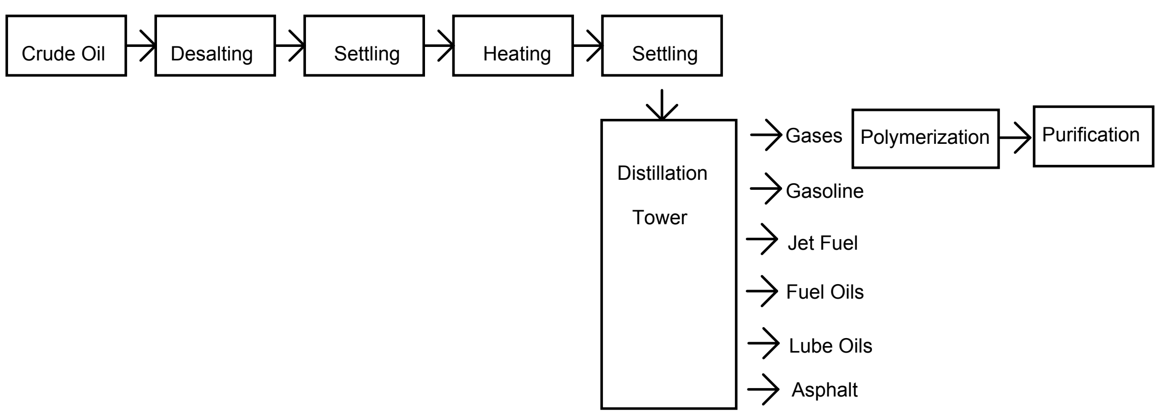
Polyethylene

Grades: 6-8 and 9-12

Science Standards: Content Standard A: Science as Inquiry; Content Standard B: Physical Science; Content Standard E: Science and Technology

Background

The ethylene (properly but infrequently called "ethene") monomer is $CH_2{=}CH_2$ and so polyethylene is $[-CH_2—CH_2-]_n$ where the monomer double bond has been "opened", enabling the carbons to join together in a long chain. Polyethylene is the most important synthetic organic (carbon based) chemical in terms of volume, sales, value and number of derivatives in the United States. The United States plastics industry produces 15 billion pounds annually. This unsaturated hydrocarbon, ethylene, is produced by "thermal cracking" petroleum. "Thermal cracking" corresponds to breaking the molecules down with heat, and then allowing the atoms to recombine into smaller units, often with double bonds. Petroleum refining to produce polyethylene has four basic steps: separation or fractionation, conversion using heat, reorganization using chemical reactions, and finishing or purifying the product. Crude oil is contaminated with 4-5% salt and so desalting and settling occurs first. Then an emulsion-breaker is added to eliminate water which is suspended in the oil. The distillation tower separates the lower molecular weight fractions from the higher ones. Steam at about 1600° C and 30 lbs/in^2 is necessary to produce low molecular weight gases. Ethane (C_2H_6) and ethylene (C_2H_4) are two of the gaseous products. Cracking of ethane to make ethylene is possible. Polymerization of ethylene and purification of the product (-65° C) to remove hydrogen gas, methane gas and ethane is the last step.



Polymerization is accomplished by heat and pressure in the presence of a catalyst. Polyethylene is an example of an addition polymerization reaction since the ethylene monomers link together to form the giant polyethylene molecules. The chain reaction typically takes place in less than a tenth of a second and releases heat. (It is an "exothermic" reaction.) The molecular weights of the polymer products vary from 10,000 to 10,000,000 amu.

The first polyethylene that was made is what we now call "low density" polyethyene, or LDPE. It is soft and waxy, flexible, and low-melting. It is used for the lids of margarine containers, for trash bags, squeeze bottles, and plastic film. The main reason that it exhibits these properties is that the polymer chains have many branches, of varying lengths, off of the main polymer backbone. These branches cause the molecule to resemble a tangled ball of yarn, and prevent the strands from arranging themselves into any kind of order.

In the 1950's, two German chemists discovered a catalyst that could prevent most of the branching that occurs when ethylene polymerizes. The new material they produced has the same chemical composition as does LDPE, but is much stronger and more rigid, as well as being more dense and higher-melting. This "high density" polyethylene, or HDPE, owes its properties to the fact that it is easier for long strands of the molecule to form ordered, or crystalline, regions than is the case with LDPE. Many packages, including milk jugs, food and bleach containers, shipping drums, and automobile gasoline tanks are made of HDPE. There were 4.2 million tons of HDPE produced in the United States in 1990.

A newer and third type of polyethylene is linear low density polyethylene, LLDPE. It is a copolymer of ethylene and 1-hexene. The branched chains from the 1-hexene attached to the polyethylene chain to provide branches of a defined length. This reduces the ease of molecular packing and gives a very low density product. Plastic film is the product most produced using LLDPE.

HDPE is readily recycled in most areas of the United States. These products are chopped into flakes, melted with coloring agents and formed into plastic lumber and wall board. Patio decks, boat docks, park benches, play ground equipment and kennels are constructed with plastic "wood". The lumber is very dense and requires screws for fastening. Of course, it is impervious to attack by insects, and is very durable.

Polyethylene is tough and quite durable. It can be extruded into films for plastic bags, shrink wrapping, and meat packaging. It can be soft and flexible as in food containers and squeeze bottles, or it can be made quite hard and rigid for storage tanks and drums. Multiple layers of polyethylene sheet is used to "line" modern landfills. It is the polymer in Tyvek® envelopes, in protective sleeves for computer disks, and in vapor barriers for home insulation. Tyvek® is a product of the Du Pont Company, where the polyethylene is formed into extremely long fibers. The web of fibers is squeezed under high pressure through a small opening to fall onto a moving belt. The belt with the fibers on top is exposed to heat and pressure so the fibers melt together. Tyvek® is a spun-bonded nonwoven fabric. It is hydrophobic or water-repellent (water will run off of it or lay in drops on its surface). Tiny pores in its structure allow gases to diffuse through, but they are too small to allow dust and bacteria to pass.

Laboratory A: Finding the Density of HDPE Samples (for high school)

Purpose: To find the density of two HDPE plastics, one from a milk jug and one from a margarine container.

Materials: for a pair of students

- 70% isopropyl alcohol
- tap water
- plastic pipet
- 100 mL beaker
- 4 small pieces of the milk jug or margarine container
  or Cool Whip Lite®(all HDPE)
- stirring rod
- electronic balance that reads to 0.01 g
- 10 mL graduated cylinder
- goggles

Density Table

Substance	Density (g/mL)
Water	1.00
(1) PETE	1.38-1.39
(2) HDPE	0.95-0.97
(3)PVC /V	1.16-1.35
(4) LDPE	0.92-0.94
(5) PP	0.90-0.91
(6) PS	1.05-1.07

Procedure:

1. Place about 35 mL of 70% isopropyl alcohol in the 100 mL beaker.
2. Add the two pieces of plastic from the milk jug and two from the margarine container (or Cool Whip Lite®). Both kinds of HDPE are more dense than the alcohol solution so they will sink to the bottom. Poke with a stirring rod to release any adhering bubbles.
3. Add small squirts of tap water, using the plastic pipet, to the beaker and stir well after each addition. Watch the behavior of the plastic pieces.
4. Repeating the addition of water will change the density of the solution by increasing it very slightly until one or both of the pieces "flinks". Flinking is when an object neither floats nor sinks but stays in the middle of the solution. At this point the object has the <u>exact</u> density of the solution.
5. When both pieces of the same container do flink, extract exactly 10.0 mL of solution using the pipet. Use a 10 mL graduated cylinder to measure the exact volume.
6. Find the mass of the 10.0 mL of solution so that you can calculate the density for the solution and for that HDPE sample. Read the balance to hundredths of a gram.
7. Continue adding water until the second sample of HDPE flinks. Measure its volume and mass as before. Calculate the density.
8.

Conclusions:

1. What are the densities for the two HDPE pieces?
2. Do they fit into the range indicated on the density table above? If not, what could cause an error to show a density of <u>less</u> than the expected range?
3. Why do you think plastics have a range for their densities and not an exact number?
4. What would happen if you put a piece of yogurt container into the 70% isopropyl alcohol solution that barely floats all four HDPE? (A yogurt container is embossed with a "5 PP".)
5. If you had two pieces of PP mixed with the four other HDPE's, how would the pieces behave if you started over with 70% isopropyl alcohol and no water?

Laboratory B: Finding the Density of HDPE Samples
(for middle level)

Purpose: To find the relative density of two HDPE plastics, one from a milk jug and one from a margarine container.

Materials: for a pair of students

- 70% isopropyl alcohol
- tap water
- plastic pipet
- 100 mL beaker
- 4 small pieces of the milk jug or margarine container
  or Cool Whip Lite®(all HDPE)
- stirring rod
- goggles

Density Table

Substance	Density (g/mL)
Water	1.00
(1) PETE	1.38-1.39
(2) HDPE	0.95-0.97
(3)PVC /V	1.16-1.35
(4) LDPE	0.92-0.94
(5) PP	0.90-0.91
(6) PS	1.05-1.07

Procedure:

1. Place about 35 mL of 70% isopropyl alcohol in the 100 mL beaker.
2. Add the two pieces of plastic from the milk jug and two from the margarine container (or Cool Whip Lite®). Both kinds of HDPE are more dense than the alcohol solution so they will sink to the bottom. Poke with a stirring rod to release any adhering bubbles.
3. Add small squirts of tap water, using the plastic pipet, to the beaker and stir well after each addition. Watch the behavior of the plastic pieces.
4. Repeating the addition of water will change the density of the solution by increasing it very slightly until one or both of the pieces "flinks". Flinking is when an object neither floats nor sinks but stays in the middle of the solution. At this point the object has the <u>exact</u> density of the solution.
5. Note which container pieces flink first. Continue adding water until the other container pieces flink.

Conclusions:

1. What are the relative densities for the two HDPE containers? Hint: Look at the density table for the six recycled plastics. Pick the approximate density numbers for the margarine container and the milk jug.
2. Why do you think plastics have a range for their densities and not an exact number?
3. What would happen if you put a piece of yogurt container into the 70% isopropyl alcohol solution that barely floats all four HDPE? (A yogurt container is embossed with a "5 PP".)
4. If you had two pieces of PP mixed with the four other HDPE's, how would the pieces behave if you started over with 70% isopropyl alcohol and no water?

Laboratory C: Physical Properties of Tyvek® and Polyethylene Bags (middle level and high school)

Purpose: To discover physical properties based upon the manufacturing processes of Tyvek® and polyethylene samples

Materials: Samples of HDPE and LDPE plastic bags from coverings for newspapers or grocery store bags or garbage bags, and Tyvek® mailing envelope

Procedure:
Cut the HDPE, LDPE and Tyvek® bags into lengthwise and crosswise pieces. Label "L" for length cut and "C" for cross cut. These should be large enough for a student to grip in both hands and pull with a steady pressure to see how easy it is to stretch and/or tear each sample. Record observations.

Type of Polymer	Lengthwise Pull	Crosswise Pull
HDPE		
LDPE		
Tyvek®		

Conclusions:
Once observations are recorded, hypothesize about the orientation of chains of molecules to help explain the observed results. The chains could be parallel to the pull, at 90 degree angles to the pull, or a mass of tangles. The pulling could involve tearing between the strands of molecule chains, or pulling at 90 degree angles to the chains or pulling on a tangled mass. Draw a sketch of the arrangement of molecule chains for each of the six pulls.

Type of Polymer	Lengthwise Pull	Crosswise Pull
HDPE		
LDPE		
Tyvek®		

Extension: Take a PS cup (polystyrene cup – clear and brittle) and crack it. Where does it crack? Why?

Teacher Notes for Finding the Density of HDPE Samples and Physical Properties

For the laboratories, make sure that you are using 70% isopropyl alcohol from a drugstore and not the 95% solution. The density of the 70% isopropyl alcohol is 0.874 g/mL. A margarine container that works for this comparison is Fleichmann's or a Cool Whip Lite® container works too. The Country Crock margarine containers we have tested have exactly the same density as a milk jug! Using a 50 mL volumetric flask to get as accurate volume measurements as possible, the density of milk jug HDPE = 0.9498 g/mL, the margarine container was 0.9558 g/mL, and the Cool Whip Lite® = 0.944 g/mL. This means that the Cool Whip Lite® samples will "flink" first upon the addition of water to the alcohol solution followed by the milk jug pieces and finally the margarine container pieces. Students must be patient and mix well with each addition of water to make the comparisons.

In using the 10 mL graduated cylinders, it was discovered that an all-glass one compared to a plastic-base cylinder resulted in unequal volumes of water. So be aware of some error in volume measurement in this lab. The density numbers may not be in the range as indicated in the table. (Conclusion question #2 HS)

Conclusion question #3 HS or #2 ML - The number of branched chains and/or crystalline regions in the polyethylene account for the differences in density.

Conclusion question #4 HS or #3 ML - The yogurt container piece would float since it is the least dense of the two polymers.

Conclusion question #5 HS or #4 ML- The yogurt container pieces would "flink" first because polypropylene is less dense than polyethylene.

Safety Concerns: Isopropyl alcohol is flammable and toxic by ingestion and inhalation. Do not have open flames near the alcohol. Have a well ventilated room. Avoid prolonged storage. Store in a dedicated "flammables" cabinet.

An assessment activity is to find the comparative densities of other plastic samples. Use a Curad® Sheer Strip and have the students identify the polymers in the strip by comparing them to the behavior of LDPE (margarine lids) and HDPE in alcohol/water solutions. Have your students start with 30 mL of 70% isopropyl alcohol and place small samples of HDPE (margarine container and milk jug) and LDPE (margarine lid) and a piece of the pull tab, and the covering over the pad of the strip, and the sheer strip itself in the beaker, then the order of "flinking" is:

first	LDPE margarine lid and covering over pad
second	HDPE milk jug
third	HDPE margarine container and pull tab
last	sheer strip never floats (It sinks in water!)

Johnson & Johnson Band-Aid® has different polymers than Curad® so the results are not as good. Students discover that the Curad® Plastic Strip has at least three kinds of polymers in it.

In the physical properties of HDPE, LDPE and Tyvek®lab, it is easiest to tear when the stands of chains are parallel to the pull as opposed to 90 degree angles to the pull. Tyvek® has random arrangement of the polymer strands and is very difficult to tear.