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#2 Investigation of Crystallinity in Polymeric Materials

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I. INTRODUCTION

Description

This series of qualitative activities provides a visual introduction to the amorphous and crystalline nature of polymers. Students will observe the inherent crystalline nature of various polymers using polarized light. Students will also compare the degree of crystallinity of low- and high-density polyethylene and polypropylene.

Student Audience

This experiment is recommended for high school chemistry students, as well as polymer and/or organic chemistry students and chemistry technology students.

Goals for the Experiment

By doing this lab the student will:

- describe the degree of crystallinity in polymers,
- explain the relationship between stress and crystallinity,
- compare the degree of crystallinity of various plastics and elastomers,
- describe how crystallinity occurs and factors which affect it,
- create crystal kaleidoscopes,
- create microscope mounts to examine crystalline nature, and
- relate crystallinity to processing and the resulting strengths and weaknesses.

Recommended Placement in the Curriculum

This experiment is recommended for use in the discussion of any of the following topics:

- molecular structure and orientation,
- crystallinity or crystalline structures,
- polyolefins,
- stress and strain, and
- intra- and inter-molecular attractions.

II. STUDENT HANDOUT

Investigation of Crystallinity in Polymeric Materials

Scenario

The Product Development Department (PDD) for Polymer Packaging Products (P^3) is working on a new container for beer. One of the considerations must be the diffusion of gases through the polymer. Ideally, oxygen (which may contribute to the spoiling of the brew) should not diffuse into the container and carbon dioxide (carbonation) should not diffuse out. Gas transmission through the polymer is one of many properties affected by the crystallinity of the polymer. Basically, the greater the crystallinity, the lower the gas transmission.

Prior to more extensive testing, PDD has decided to look at polymer formulations already produced by the company to determine which, if any, have the required crystalline morphology (form and structure) to minimize gas transmission. As a chemical technician, it is your job to prepare the samples of different polymers for observation and comparison of their crystallinity.

Industrial Applications

Density and crystallinity are several of the more important characteristics influencing the end use properties of products made with polyethylene (PE). These two properties are related because when polymers are crystalline it is generally due to a uniformity and compactness of the molecular chains, which also help to determine density. Thus higher crystallinity usually results in higher density, stiffness, and tensile strength. In manufacturing, high stiffness may result in thinner walled bottles or articles and faster injection cycles (including injection, die close, and die open time), that gives them an economic advantage. Higher crystallinity also results in better barrier properties for gas (e.g., O_2) and liquid transmission. This is important for food and beverage containers and food wrap. On the other hand, flexibility is desirable in applications such as polyethylene pipe and tubing, plastic grocery bags, and squeeze bottles for lotions, shampoos, etc. In most applications, a balance of barrier properties will be needed.

Background

Polymers are either amorphous or semicrystalline. They can be described as having a degree of crystallinity which can be affected by many factors. Crystallinity results in part because molecules or portions of polymer chains form highly organized areas called spherulites which are interspersed in the solid matrix. Spherulites are made up of fibrils which radiate from a common center. The fibrils consist of lamellae which are formed by the folding of the polymer chains. (See Figure 1.)

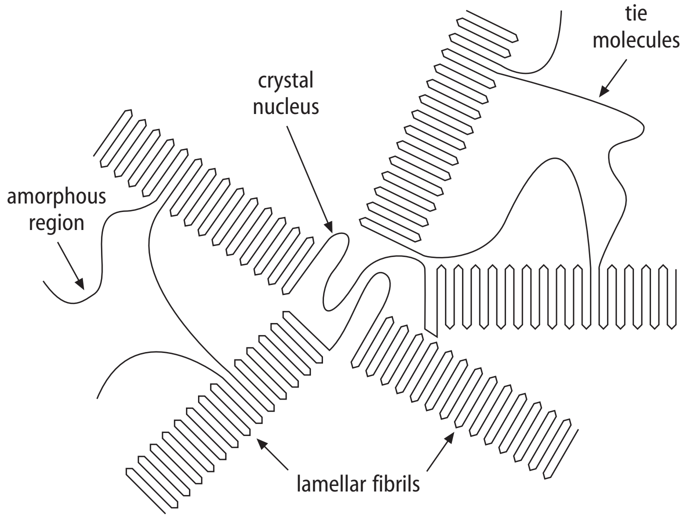


Figure 1: A Polymer Crystalline Spherulite

Polymers will have a certain degree of crystallinity inherent to them but the degree of crystallinity can be affected by aging, the heat history of the material, the polymerization process, molding process, or stress in service use. The degree of crystallinity of a polymer will also result in variance of physical properties. For example, in polyethylene, as the crystallinity increases tensile strength increases but clarity decreases. As a polymer is stressed due to molding processes, or even simple stretching, the crystallinity of the material will be altered and physical properties changed. The first two activities will allow students to see crystalline areas in sheet or molded materials which appear to be amorphous. They will also stress material to see how the crystallinity of the material is altered. The third activity will look at the inherent degrees of crystallinity in low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP). These activities are also based on the principles of light and polarization. Light energy is transmitted by magnetic and electric vibrations in all directions through space. When using two sheets of polarizing material the first sheet blocks all the rays of light in one direction. If the second polarizer is turned perpendicular to the first then all light rays are blocked. When a material containing crystals is placed between the two polarizers, the filtered light hits the crystalline areas which refract the polarized light, as well as slowing down the wavelengths and frequencies of light which results in various colors being transmitted through the second polarizer.

Safety, Handling, and Disposal

- While the chemicals and procedures in this experiment may not be unduly hazardous, proper laboratory safety precautions are absolutely necessary.
- In the second investigation, the hotplate and the slides will be very hot. Be careful when handling, and use heat-resistant gloves or tongs. To avoid burns, use a tongue depressor to sandwich the plastic.

Materials

Investigation #1

Per student

- 3-inch x 5-inch sheet of construction paper, card stock, or poster board
- 2 1-inch squares of polarizing material

Per group

- compass or templates for drawing circles
- scissors
- very inexpensive cellophane tape

Investigation #2

Per group

- hot plate
- glass microscope slides (heat tempered)
- wooden tongue depressors
- LDPE, HDPE, and PP pellets or ½-inch squares of each type of film
- two 2-inch squares of polarized sheet
- heat-resistant gloves or tongs
- microscope

Procedure

Investigation #1

This activity will use the principles described in the introduction and observed in the demonstration to create a kaleidoscope from inexpensive tape and heavy paper.

1. Cut one circle of paper 2.5 inches in diameter with a ⅝- to ¾-inch hole in the center. Cut a second circle 2 inches in diameter, also with a center hole.
2. With the circles flat on a table, place a 1-inch square of polarizer over each center hole.
3. Tape the polarizers to the paper circles covering the entire surface of polarizer. The more tape used and the more varied the directions that the tape is placed, the more varied the colors that will be seen.

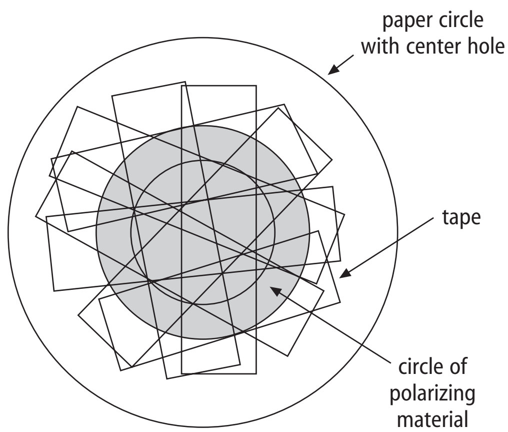


Figure 2: Kaleidoscope Dish

4. Place taped sides of the circles together and look through the center hole. As the disks are rotated, a myriad of colors will be visible.

Investigation #2

This activity investigates the differences in inherent crystallinity of low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP).

Be careful, the hot plate and slides will be EXTREMELY HOT!

1. Warm 2 glass microscope slides on a hot plate. Place one pellet or a ½-inch square of LDPE, HDPE, or PP film on one slide. As the pellet softens, remove it from the hot plate using heat-resistant gloves or tongs and immediately sandwich the plastic with the other glass slide. Press straight down or twist slightly as the second slide is pressed into place using the tongue depressor.
2. Prepare a microscope by placing one polarized sheet on the microscope stage. A second polarizer should be perpendicular to the first (and will be on top of the slide while viewing).
3. Move the polarizers relative to each other until the field is dark. Slip a cooled slide with a polymer sample onto the stage between the two pieces of polarized sheeting to view the patterns of crystallinity. Examine the sample for spherulites starting with a low magnification. The larger spherulites are usually found on the edge in a thinner section of the sample. Note the difference in degrees of crystallinity between the different materials.

Questions

1. Explain the difference between the behavior of a plastic and that of an elastomer as each is stretched.
2. Corners of containers and bottles tend to be the weak areas of an object and will break more readily when impacted than the flatter surfaces. Explain this based on crystallinity in the molding process.
3. Describe what is happening on the molecular level when a stretched plastic necks.

4. Describe the differences in degree of crystallinity between LDPE (low- density polyethylene), HDPE (high-density polyethylene), and PP (polypropylene) and relate these to structural differences.

III. INSTRUCTOR NOTES

Investigation of Crystallinity in Polymeric Materials

Purpose

The following qualitative activities will use polarized light to investigate the inherent degree of crystallinity in a variety of polymers. These activities will also introduce the various factors which affect crystallinity including stress. The relationship between processing techniques and crystallinity will also be addressed.

Time Required

Demonstration #1 and Investigation #1 together can be completed in one 50-minute class period. They can be used to augment classroom discussion or as a lab activity on crystallization or polarized light. Investigation #2 could be completed in one 50-minute class period depending on the number of samples used and the number of microscopes available. In a high school classroom you may want to prepare slides one day and look at them under the microscopes the next.

Suggested Group Size

Demonstration #1 can be done in a small classroom or a large lecture hall. Investigation #1 can then be done as an individual activity. Investigation #2 works well for pairs or small groups. Completed slides of different materials can be shared among groups.

Materials

Demonstration #1

Per class

- polarized sheets (2 pieces 7-8 inches square)

> *Polarizing film is available from Edmund Scientific Company, Industrial Optics Division, 101 East Gloucester Pike, Barrington, NJ 08007-1380; 1-609-573-6250; industrialsales@edsci.com; http://www.edsci.com. The industrial surplus experimental quality is the most practical: stock number P37,350 for a 7.5-inch square, about $10.*

- overhead projector
- projection screen or white wall
- clear plastic film (freezer bags work best)
- six-pack ring holder (copolymer of 99% ethylene and 1% carbon monoxide)
- clear polystyrene containers (petri dishes, deli containers, clear cutlery, latex bands or gloves, reaction plates, PE pipettes)
- latex glove or tourniquet strap

Investigation #1

Per student

- 3-inch x 5-inch sheet of construction paper, card stock, or poster board
- 2 1-inch squares of polarizing material

Per group
- compass or templates for drawing circles
- scissors
- very inexpensive cellophane tape

➤ *More costly tape will not work.*

Investigation #2

Per group
- hot plate
- glass microscope slides (heat tempered)
- wooden tongue depressors
- LDPE, HDPE, and PP pellets or ¼-inch squares of each type of film (or groups can use one type and share results)

➤ *See "Procedural Tips" for additional suggestions.*

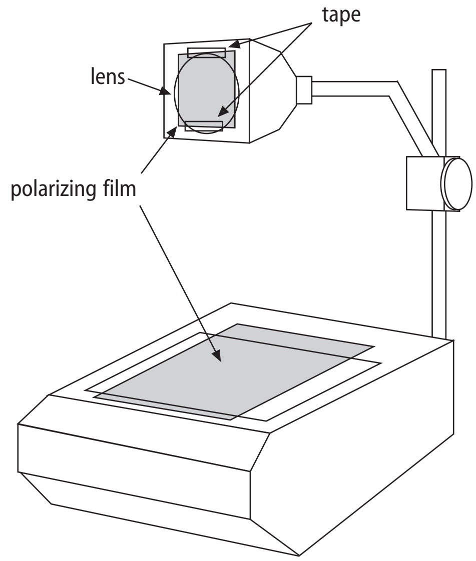
- two 2-inch squares of polarized sheet
- heat-resistant gloves or tongs
- microscope

Procedure

Demonstration #1

This simple demonstration will show the inherent crystallinity of transparent plastic objects. Besides the inherent crystallinity, the projected colors that result indicate various things such as the freeze lines, the flow pattern of an injection molded part, or the increased crystallinity due to stress.

1. Tape one piece of polarized sheeting over the head of the overhead projector so that the light passes through it. (Be careful as this piece may begin to char if the light is left on too long.) Then lay the second polarized sheet on the top surface of the overhead. You need to rotate this piece of sheeting so all the light is blocked out when the overhead is on.



2. Turn the overhead on and place one 1-inch x 4-inch sample of film (from a freezer bag) on top of and diagonal to the polarized sheet. Note that you will barely be able to see the sample projected on the screen.
3. Slowly stretch the film and notice how the stress creates areas of crystallinity. If you continue to stretch the film until all the molecules are oriented and crystalline, the colors will diminish and be seen only along the lines of orientation. Stretch pieces of film both with the grain and against the grain and observe the differences. The sample stretched perpendicular to the grain, if pulled slowly, will reorient the molecules in the direction of your pulling. You will also observe a narrowing which is called "necking."
4. Repeat with the six-pack ring, noting that there are already areas of stress and crystallinity from the molding process.
5. Repeat with various styrene containers, pipettes, clear plastic compasses, etc. Note how bends, corners, and holes correspond to the brightest colors.
6. Using a piece of latex sheeting or a glove, stretch and relax the material, observing the differences in the stressed and relaxed conditions.

Safety, Handling, and Disposal

- While the chemicals and procedures in this experiment may not be unduly hazardous, proper laboratory safety precautions are absolutely necessary.
- In Investigation #2, the hot plate and the slides will be very hot. Be careful when handling and use heat-resistant gloves or tongs. To avoid burns, use a tongue depressor to sandwich the plastic.
- Do not use PVC or PVDC films since heating at elevated temperature could result in hydrogen chloride gas being released.

Points to Cover in Pre-Lab

- Demonstration #1 and Investigation #1 can be used along with discussion of the topic, or as a pre-lab for lecture. The wider the range of products used to demonstrate the crystallinity in processed objects, the better the students will identify sources of stress and flow patterns (e.g., corners, rounded molds, cutlery, bottle bottoms).

- Demonstrate the technique in for Investigation #2, reminding the students that the danger of serious burns from the hot plate and hot slides is very possible. Molten polymers tend to ooze out from between the glass slides.
- Do not overheat and burn the polymers.

Procedural Tips and Suggestions

- Be certain to have both polarizers in place when the overhead is turned on. The heat produced is sufficient to deform and burn the polarizer if the stage polarizer is removed while the head polarizer is left in place.
- Try the tape before purchasing large quantities to be certain it has a high degree of crystallinity for Investigation #1.
- For Investigation #2, practice beforehand to choose plastics that melt readily. LDPE will melt quickly and spread nicely. HDPE and PP with a melt index of 6 g/10 min or higher will work best. (The higher the melt index, the more easily the polymer will flow.) Note that the pellets need to be non-pigmented for this activity to work. You can also try Saran Wrap or slivers from a clear soda bottle (PETE, polyethylene terephthalate). If your students have trouble getting a layer which is thin enough, have them melt the plastic between the two microscope slides with some weight on top.
- Be careful, the hot plate and slides will be EXTREMELY HOT. Remind students regularly to use caution and thus avoid severe burns!

Plausible Answers to Questions

1. Explain the difference between the behavior of a plastic and that of an elastomer as each is stretched.

A: Both plastics and elastomers can be stretched. The difference is that elastomer will stretch with little to no permanent deformation whereas plastics will deform once stretched. This can be seen when samples of each are stretched. Also, stretching causes the polymer chains of both materials to align and become more crystalline as indicated by the increase in color when stretch between two polarizers. The latex sheet will crystallize then relax and become more amorphous over and over again.

2. Corners of containers and bottles tend to be the weak areas of an object and will break when impacted more readily than the flatter surfaces. Explain this based on crystallinity in the molding process.

A: Various samples show increased crystallinity along the corners by increased patterns of color when viewed between two polarizers. These are areas which were stressed during processing whether injection molded, blow molded, or thermoformed. The engineering of molds and molding processes are extremely critical to make a container in the shape desired while limiting the areas of stress and crystallinity which result in weak spots in the product.

3. Describe what is happening on the molecular level when a stretched plastic necks.

A: When a plastic is stretched slowly perpendicular to the direction of extrusion or anisotropy, the polymer chains are given time to reorient along the direction of stress. As the polymer reorients, the area narrows or necks. On the other hand, if the plastic is stretched rapidly, the orientation does not have time to occur and the stress overcomes the intermolecular attractions resulting in the sample breaking quickly with limited or no necking.

4. Describe the differences in degree of crystallinity between LDPE, HDPE, and PP and relate these to structural differences.

A: Answers will vary with the samples tested. Generally, LDPE will be less crystalline than HDPE which is less crystalline than PP. LDPE has branched chains and results in a lower density, lower packing, and fewer spherulites. HDPE has more linear shaped chains which allow for closer packing which results in greater degree of crystallinity. PP is approximately ninety-five percent isotactic (the methyl groups are oriented on the same side of the polymer backbone) which allows for closer packing and a greater degree of crystallinity. You may also notice that melt flow, flexibility, permeability, and clarity decrease as the crystallinity of these polymers increase. Melting point, tensile strength, and impact strength increase with increased crystallinity.

References and Acknowledgments

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