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#3 The Study of Molecular Orientation by Linear Dimension Change of Polymeric Films

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I. INTRODUCTION

Description

This lab will provide students an opportunity to investigate the linear dimension change of heated plastic film and relate the results to processing and service use of the materials. Students will cut samples from film and prepare them for testing. The students will make pre- and post-measurements to calculate percent change in dimension as related to anisotropy (differences in properties according to the direction of measurement) and molecular reorientation.

Student Audience

This investigation is appropriate for high school chemistry students, polymer and/or organic chemistry students, and chemistry technology students

Goals for the Experiment

The student will:

- prepare and measure samples with accuracy and precision,
- calculate percent changes from measurements,
- locate and describe anisotropic nature (line or direction of extrusion) in films,
- (optional) create a data chart for expected data,
- relate results to commercial applications,
- describe changes on the molecular level using data obtained,
- compare and contrast results based on polymeric content and use, and
- describe the effects of heating on molecular orientation of polymers.

Recommended Placement in the Curriculum

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

- molecular orientation,
- effects of heat,
- polymers, and
- statistical analysis of data including accuracy and precision.

II. STUDENT HANDOUT

The Study of Molecular Orientation by Linear Dimension Change of Polymeric Films

Scenario

The Handy-Dandy Hardware chain recently introduced a house brand of shrink insulation for windows. Unfortunately, an unexpectedly high percentage of the packages sold have been returned. Customers claim that the insulation does not shrink by the expected amount when it is heated according to the package directions. The customer service department at Handy-Dandy has demanded that the supplier of the film, Frivolous Film Company, look into the problem.

As an employee of Frivolous Film, you have been assigned to test the validity of the complaints. To do this, you have decided to test the shrinkage both length- and width-wise at various temperatures. Hopefully this will help you to focus on the source of the problem which might be the formulation of the shrink insulation, the instructions for use on the package, or the amount of heat applied by the customers.

Industrial Application

Various polymeric films are produced in a manner which specifically orients molecules for use in industrial applications such as shrink wrap and merchandise bags for packaging and for purposes of insulation. Depending on the intended application, the molecules are frozen in a stressed orientation with the direction of extrusion of the film prepared so the stress is both parallel and perpendicular (biaxial orientation) to the direction of extrusion. The nature of this orientation is a complex function of molecular structure and processing conditions such as the blow up ratio of the film bubble. This activity, based on ASTM D-1204, will allow students to quantitatively determine the percent change in the linear dimensions of plastic films and assess the results in relationship to their intended application. This accelerated aging test investigates the changes in samples at a fixed time interval but increasing temperature, whereas other tests (ASTM D-2115) will accelerate the testing by using a single high temperature and increasing time interval to determine aging.

Shrink wrap is generally just stretched polyethylene although copolymers such as polyethylene-vinyl acetate (EVA) may be used in some applications. Food wrap is usually a multi-layer film with an inner oxygen (O_2) barrier of nylon or EVOH bonded to the outer PE or PP layers with an adhesive.

Safety, Handling, and Disposal

While the chemicals and procedures in this experiment may not be unduly hazardous, proper laboratory safety precautions are absolutely necessary.

- Care should be taken when placing samples in and removing them from the ovens to prevent burns.
- Samples should be allowed to come to room temperature after being removed from the oven (15-20 minutes) before handling.

- Do not use PVC or PVDC films since heating at elevated temperature could result in hydrogen chloride gas being released.
- Do not let polymers come into contact with the oven, especially the heating element of the toaster oven.

Materials

Activity #1

- polyethylene film samples such as shrink window insulation, other shrink wrap, polyethylene sheeting, food wrap, or merchandise bags
- brown paper bags cut to approximately 15 cm x 30 cm (one rectangle per sample)
- 4 paper clips per sample
- baby powder or talc
- scissors
- permanent marking pens
- ruler graduated to 0.1 cm
- oven which will reach and hold temperatures from 50 °C to 150 °C (within ±10 °C)
- data chart
- (optional) micrometer (+/- .01 mm)

Activity #2

- clear polystyrene lids from yogurt containers, clear rigid bakery or deli containers, salad lids from fast food restaurants
- scissors
- permanent markers
- foil baking sheets or foil lined cookie sheets
- oven which will reach and hold temperatures of about 120 °C

Procedure

Activity #1

Various plastic films are made such that when heat is applied they will shrink to fit the object being wrapped. This may be meat on a foam tray in a grocery store, multiple boxes being prepared for shipping, or a commercial package that is being sealed for safety or freshness. Another application is films made for window insulation that is applied to a window with adhesive tape and then a blow dryer is used to shrink the material to a tight fit. Film of this type is also sold seasonally to wrap and then shrink around Easter or gift baskets. In each of the cases the material must shrink without loss of clarity although in the first applications films tend to shrink along the line of extrusion while the second application the material needs to shrink uniformly in both directions.

1. Preheat the oven to 50 °C (105 °F). For additional testing, preheat to 100 °C or 150 °C. (212 °F or 320 °F).

2. Note the grain of the film to be tested by holding the film up to the light. The grain should be visible as striations, streaks, or lines in the film in the machine direction, the direction the polymer was extruded. Mark this with an arrow as the direction of extrusion. (This also indicates the orientation of the majority of polymer chains in the sample.)
3. Cut 10 cm square samples from the material, marking the midpoints of both sides and the direction of extrusion. Cut samples from both the center of the sample and the edge, marking them appropriately. Make the midpoint marks at least 1 cm in length. See Figure 1.

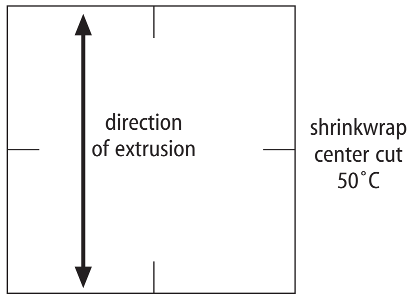

Figure 1. Cut a 10-cm square sample, mark the direction of extrusion and the midpoints of the sides.

4. Measure the exact distance, + or - 0.1 cm, from the midpoints both parallel and transverse to the direction of extrusion. Record on data chart (sample provided).
5. Fold the piece of brown paper bag in half so that it is about 15 cm x 15 cm.
6. Sprinkle baby powder or talc inside the folded paper and smooth it to coat the surface completely. (This allows the film to change dimensionally without restriction during the heating process.)
7. Place one film sample between the powdered sides of the paper. Be certain the film lays flat and does not have any folds or creases in it.
8. Paper clip the edges of the paper to keep the film from falling out but do not clip the plastic sample.
9. Carefully place the samples in the preheated 50 °C oven so they do not overlap. Leave for one hour and then remove from the oven and cool for 10-15 minutes. Use heat resistant gloves when putting samples in and out of oven.
10. Remove the sample and measure between the midpoints both transverse and parallel to the direction of extrusion.
11. Calculate the percent linear change for each set of measurements using the following equation:

$$\frac{\textit{Final dimension} - \textit{Initial dimension}}{\textit{Initial dimension}} \times 100 = \textit{\% Linear Change}$$

12. Analyze results by pooling the class data and determining averages and standard deviations. Also, conduct t-tests where appropriate to identify data which can be rejected. Then consider the following:

a. Were there variations in change between center and edge pieces? If there are differences in the percent linear change, how would this effect the service performance of the material?

b. Were there differences between the dimension changes transverse to the direction of extrusion and parallel to the direction of extrusion?

c. What is occurring on the molecular level when the film is heated?

d. Investigate the service conditions (the conditions under which it might be used) of the film you tested. How does your data relate to these service needs?

13. Repeat the experiment at 100 °C and at 150 °C. If material begins to smoke during testing lower the temperature or remove and discontinue the testing.

14. (optional) Measure the thickness of a control sample, the 50 °C sample, the 100 °C sample, and the 150 °C sample using a thinness gauge to + or -0.01 mm. Describe what happened to the materials as the temperature increased.

<u>Activity #2</u>

This activity brings back a childhood craft kit based on the same principles as in Activity #1: Shrinky Dinks®.

1. Use clear polystyrene containers or lids and cut in squares or circles. Mark with designs using permanent markers.
2. Place on a foil covered tray and bake in a 250 °F (120 °C) oven. Use heat resistant gloves when putting tray in and out of the oven.
3. Check every minute until the sample stops shrinking.
4. Remove from oven, allow to cool, and remove medallion from the foil.

Questions

1. What is occurring in the sample when it shrinks only along the line of extrusion (the machine direction)?
2. What happens when biaxially oriented films shrink?
3. Is the precision of the data sufficient to determine whether your edge and center results are statistically significant?
4. What causes the loss of clarity in the films (aside from the talc adhering to the polymer)?
5. Would you expect the mass of the sample to change when heated? Why or why not?
6. Why do the films thicken upon heating?

References

1986 Annual Book of American Society for Testing and Materials Standards, Volume 8.01 "D-1204 Standard Test Method for Linear Dimensional Changes of Non-rigid Thermoplastic Sheeting of Film at Elevated Temperature"; ASTM: Philadelphia, PA; pp. 847-852.

1986 Annual Book of American Society for Testing and Materials Standards, Volume 8.02 "D-2115-67 Standard Practice for Oven Heat Stability of Poly (Vinyl Chloride) Compositions"; ASTM: Philadelphia, PA; pp. 252-254.

Data Chart 1 for Linear Dimension Change				
T = 50° C	Edge		Center	
	parallel	transverse	parallel	transverse
Initial Dimension				
Final Dimension				
% Change in Dimension				

Data Chart 2 for Linear Dimension Change				
T = 100° C	Edge		Center	
	parallel	transverse	parallel	transverse
Initial Dimension				
Final Dimension				
% Change in Dimension				

Data Chart 3 for Linear Dimension Change				
T = 150° C	Edge		Center	
	parallel	transverse	parallel	transverse
Initial Dimension				
Final Dimension				
% Change in Dimension				

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III. INSTRUCTOR NOTES

The Study of Molecular Orientation by Linear Dimension Change of Polymeric Films

Purpose

In these laboratory activities, you will investigate the behavior of plastic films when heated. The results can be used to determine if the various films are appropriate for their intended commercial use. Data can also be used to determine variations caused by processing.

Time Required

Sample preparation will take approximately one hour provided that data charts are ready for the recording of sample dimensions. Heating takes one hour in a pre-heated oven. The time frame will vary with the number of ovens you have available. Three ovens each set at different temperatures is optimum. You may also choose to do the heating on your own outside of lab time. Measurements and calculations will take an additional class period.

Even though the ASTM suggests that samples should not overlap, for a class project overlapping does not have too drastic of an effect on results.

Suggested Group Size

This can be done as independent investigation, in small groups, or each individual in a class can do samples at each temperature. The number and size of ovens will be a key factor in time frame and how many students can complete this concurrently.

Materials

<u>Activity #1</u>

- polyethylene film samples cut into 6-10 cm squares such as shrink window insulation, other shrink wrap, polyethylene sheeting or food wrap. 3 will be cut from the edge of the sample and 3 from the center.
- brown paper bags cut to approximately 15 cm x 30 cm (one rectangle per sample)
- 4 metal paper clips per sample (not vinyl coated)
- baby powder or talc
- scissors
- permanent marking pens
- ruler graduated to 0.1 cm
- oven which will reach and hold temperatures from 50 °C to 150 °C (within ±10 °C)
- data chart (sample provided)

<u>Activity #2</u>

- clear polystyrene lids from yogurt containers with colored edge cut off, clear rigid bakery containers, salad lids from fast food restaurants.
- permanent markers in various colors
- foil baking sheets or foil lined cookie sheets
- scissors
- oven which will reach and hold temperatures of about 120 °C (a toaster oven works well here)

Safety, Handling, and Disposal

While the chemicals and procedures in this experiment may not be unduly hazardous, proper laboratory safety precautions are absolutely necessary.

- Care should be taken when placing samples in and removing them from the aging ovens to prevent burns.
- Also samples should be allowed to come to room temperature after being removed from the oven (15-20 minutes) before handling.
- Do not use PVC or PVDC films since heating at elevated temperature could result in hydrogen chloride gas being released. The most common chlorinated film is Saran wrap for the microwave. To check for chlorine: Heat a bare copper wire in a Bunsen burner flame until incandescent. Touch the hot wire to the plastic sample several times and return wire to the flame. If a green flame is produced there is chlorine present and the film should not be used.

Points to Cover in Pre-Lab

- Discuss the film blowing process.
- Walk students through determining the anisotropy of their film samples by holding the sample up to a light and look for the grain. Heat shrink wrap may be difficult to determine, therefore choose a direction as a reference point. Shrink wrap may be pseudotropic which means there is no distinct grain.
- Discuss the factors that influence chain orientation in polyethylene film. For example, many polyethylene films are produced using a blowing system. The solid polymer with its many long coiled strands is heated until it melts. The melt is extruded uniformly through a round slit in a metal die to produce a thin tube. The leading edges of the tube are then forced together to form a bubble. Compressed air is blown into the tube so fast that the bubble expands outward both parallel to and perpendicular to the machine direction, stretching the polymer strands. The bubble cools, locking the strands into their stretched-out configurations, and collapses into a flat, two-layer sheet.
- Review anisotropy and its relationship to this activity.
- Remind students to mark samples prior to testing and make measurements from midpoints only.
- Discuss accuracy, precision, and statistics (hypothesis testing and student’s t-test).

Procedural Tips and Suggestions

- Care must be taken during sample preparation to keep the talc or baby powder contained. Students tend to use excessive amounts of powder and, although your lab will have a pleasant odor, the powder will cause slick surfaces on counters and floors. You may choose to do this in a fume hood to help limit the problem. Sample preparation is critical. Remind students to be careful in measuring and marking the samples.
- Do not leave heating plastics unattended! Although rare, some plastics will overheat and begin to smoke. HDPE will sometimes melt. If either occurs, shut ovens off immediately and readjust temperatures for the study.
- Step 12: Analyze results considering the following:

a. During the extrusion process the edges of the film may be thinner, stretched, or oriented differently from the center of the film. As a result, the edges may have greater linear dimension changes. In many film applications, like a trash bag, this will have no effect but in an application such as a cooking bag additional linear changes could result in the bag shrinking too much for the food in it.

b. This will depend on the film used. Some will have the same dimensional change in both directions as in window insulation shrink film. Others will have a much greater dimensional change in one direction than in the other. The amount of stretch during processing will also effect this.

c. The polymers that have been oriented and stretched during the extrusion process can relax as the material warms and begins to flow. If the heat is sufficiently high, crystallinity may increase and the clarity of the film will decrease.

d. Answers will vary with film, results, and service use.

- Step 13: Depending on the dimensional change, the thickness will increase. (The mass will remain constant).
- You may want to look at cigarette package wrap which may be biaxially oriented polypropylene.
- You could analyze films by IR or NMR to determine types.

Sample Results

Data Chart 1 for Linear Dimension Change				
Material: polyethylene food wrap				
T = 50 ° C	Edge		Center	
	parallel	transverse	parallel	transverse
Initial Dimension	15.0 cm	14.0 cm	15.1 cm	14.9 cm
Final Dimension	14.8 cm	14.4 cm	14.9 cm	14.5 cm
% Change in Dimension	-1.3%	-3.4%	-1.3%	-2.7%

These results indicate that heating caused the molecular chains to relax as indicated by the –1.3% change. There is greater shrinkage in the direction transverse to anisotropy which indicates that molecules are relaxing and becoming more compact and crystalline even though the clarity remained unchanged in both samples. The edge sample shrank more indicating that this area may have been stretched and stressed more during processing than the center sample.

Data Chart 2 for Linear Dimension Change				
Material: window cover				
T =100° C	Edge		Center	
	parallel	transverse	parallel	transverse
% Change in Dimension	-31%	-35%	-33%	-35%

Data Chart 3 for Linear Dimension Change				
Material: sandwich bag				
T =100° C	Edge		Center	
	parallel	transverse	parallel	transverse
% Change in Dimension	+20%	-40%	+10%	-30%

Plausible Answers to Questions

1. What is occurring in the sample when it shrinks only along the line of extrusion (the machine direction)?

A: In this situation the polymer was stretched and stressed during production along the line of extrusion causing the molecule chains to generally orient in this direction and become frozen in a stretched out fashion. When heat is applied the stress is relieved and the molecules are able to relax causing the shrinking effect. The more stress that was applied during processing the greater shrinking will occur along the machine direction.

2. What happens when biaxially oriented films shrink?

A: The heating relaxes the molecules allowing them to reorient equally in both directions and return to their preferred random orientation. Entropy is the driving force for the film shrinkage.

3. Is the precision of the data sufficient to determine whether your edge and center results are statistically significant?

A: The answer to this question will vary. Pooling class results to provide multiple pieces of data will normally increase precision.

4. What causes the loss of clarity in the films (aside from the talc adhering to the polymer)?

A: The degree of crystallinity is frozen into the film during processing. As the heating occurs, the molecules may go beyond relaxing to the point of orienting in a more crystalline fashion. As crystallinity of a plastic sample increases, the transparency diminishes.

5. Would you expect the mass of the sample to change when heated? Why or why not.

A: For most films, the mass will not change with heating even though the dimensions of the sample change. This is because while there is a rearrangement of the polymer strands, nothing is being lost.

6. Why do the films thicken upon heating?

A: Since the shrinking of the length and width of the film is a physical change, the thickness must increase to compensate if the mass and volume are to remain constant.

References

1986 Annual Book of American Society for Testing and Materials Standards, Volume 8.01 "D-1204 Standard Test Method for Linear Dimensional Changes of Non-rigid Thermoplastic Sheeting of Film at Elevated Temperature"; ASTM: Philadelphia, PA; pp. 847-852.

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