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#7 Water and Polymers

Submitted by: Melanie Stewart, Stow-Munroe Falls High School, Stow, OH 44224

I. INTRODUCTION

Description

These activities represent both qualitative and quantitative investigations based on the interaction between water and various polymers. Hydrogen bonding between water and different polymers is the basis of the investigations. Students will determine the percent moisture contained in various plastics along with a qualitative procedure to determine if water is present in a plastic sample. Students will also perform a modified industrial test to determine the percent moisture absorbed by various plastics.

Student Audience

This lab can be used with high school chemistry students, as well as, polymer and/or organic chemistry students, and chemistry technology students

Goals for the Experiment

The student will:

- calculate percent moisture for plastics,
- perform a Thomasetti Volatile Index (TVI) for plastics,
- calculate the percent moisture absorbed, taking into consideration soluble matter lost,
- describe hydrogen bonding,
- project hydrophobic and hygroscopic nature by atomic composition of polymers,
- relate percent moisture and water absorption to atomic composition of polymers,
- discuss accuracy and precision of test results compared to known values,
- explain how additives affect the hydrophilic and hydrophobic nature of materials, and
- compare and contrast plastics in various service applications based on their response to water.

Recommended Placement in the Curriculum

These investigations can be used in conjunction with

- units on water or polymers,
- discussion of intermolecular attractions and hydrogen bonding, and
- for experience with the concepts of accuracy and precision.

II. STUDENT HANDBOOK

Water and Polymers

Scenario

Damp Dirt is an agricultural product designed to help with water retention in soils. A major chain of discount stores has been marketing Damp Dirt for your company. However, they are now considering taking it off their shelves because of customer complaints that the claims regarding water retention made on its label are not valid. As a chemical technician in the Quality Assurance Lab of the agricultural products company which manufacturers Damp Dirt, your job is to determine the validity (or lack of validity) of the complaints. For this evaluation, you use retained samples of the lots which garnered the most complaints. (Retain samples are samples of products kept by a company in case future testing is needed.) One major part of your work will be to establish the maximum amount of water that Damp Dirt can hold as a percentage of its weight.

Industrial Application

Polymers will react to water based on their elemental composition as well as the various additives that are compounded into the base polymer. In general, hydrogen bonding occurs between the hydrogen of water and the unshared electrons of nitrogen and oxygen. Polymers containing only C and H, or C, H, and halogens tend to repel water and are described as hydrophobic. Common C and H polymers include the polyolefins such as polyethylene and polypropylene, and polystyrene. Polymers containing chlorine such as polyvinylchloride, neoprene, and chlorinated polyethylene are also hydrophobic. Polymers containing O or N attract water and are described as hygroscopic or hydrophilic because the unshared electrons of N and O will attract the hydrogens of the water molecules.

In the industrial setting, water poses tremendous problems in the molding of products from nitrogen and oxygen containing polymers such as poly(ethylene terephthalate), nylons, ABS, or polyformaldehyde. These materials must be dried before molding or surface marks and weak weld lines (where several pieces come together to make the product) may result. Hydrophilic materials may also have changes in physical and mechanical properties when water is absorbed. Additives will affect a polymer's reaction to water. Some additives will absorb water and others will dissolve out of the polymer. The following investigations will present ways to look at the interaction of water with polymers.

Safety, Handling, and Disposal

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

- Be careful when handling hot materials in the oven or on hot plates.
- Use heat resistant gloves or tongs as indicated.
- Use a tongue depressor to sandwich the plastic to avoid burns when completing the TVI test.

Materials

Investigation #1

- 1–2 grams plastic pellets
- oven

- heat resistant gloves
- foil pans or glass 50-mL beakers (1 for each sample)
- analytical balance
- desiccator
- (optional) hot water

Investigation #2

- various plastic pellets
- 2 glass microscope slides per sample
- hot plate
- wooden tongue depressor
- (optional but very useful) magnifying glass
- tongs

Investigation #3

- polyacrylamide crystals
- analytical balance
- distilled water
- sandwich size ziptop freezer bags
- foil 8- or 9-inch cake pans
- oven
- dessicator

Procedure

Investigation #1: Percent Moisture

Some polymers will absorb water from the air, causing polymer processors to spend millions of dollars each year to dry plastics. This quantitative investigation will provide a simple look at the inherent moisture contained in various polymers.

1. Tare a pan or beaker and then transfer 1–2 grams of plastic pellets to the pan.
2. Record the mass to nearest 0.001 g as the initial mass.
3. Repeat for each type of pellet used.
4. Dry for 24 hours at 50 °C or 1 hour at 100 °C. (If using 100 °C oven use heat resistant gloves to avoid burns when putting in and taking out samples.)
5. Remove from oven and cool in the charged desiccator for 20-30 minutes.
6. Remass the pellets to the nearest 0.001 g and record as the final mass. Calculate the percent moisture as follows:

$$\frac{\text{initial mass} - \text{final mass}}{\text{initial mass}} \times 100 = \%\ \text{moisture}$$

* If your answer is negative, an error was made since under these circumstance moisture should not be gained.

7. (optional) Repeat the procedure, drying for longer periods of time and leaving in dessicator longer to ensure that room temperature is reached. Are the results any different? Repeat but soak the pellets in water for 24 hours first. Also repeat but soak the pellets in hot water first. Compare the results with the initial investigation.

Investigation #2: TVI

TVI is an industrial test which stands for the Thomasetti Volatile Index. This is a qualitative test that will determine if moisture is present in a pellet. The drying process in the previous investigation would drive away both trapped moisture and surface moisture. The TVI will indicate only moisture that is trapped in the plastic pellet.

1. Heat the hot plate at medium to high setting.
2. Lay 2 slides on the hot plate and place two of the same type pellet on one slide. **Be cautious when using the hot plate. Severe burns can result when touching its surface or the materials heated on it.**
3. As the pellets soften, sandwich them with the second heated slide, pressing straight down with the wooden stick. (Slides can be removed and sandwiched on the counter to decrease risk of burns and overheating of the pellets.)
4. Each pellet should form about a 1/2 inch circle. If the pellet scorches, try again with the hot plate at a lower temperature. If the slide does not readily spread the pellet, let it heat longer.
5. Use the tongs to carefully remove the slide and let it cool completely.
6. Count the number of bubbles trapped in the plastic. These indicate trapped water.
7. Repeat with a variety of other plastics.

Investigation #3: Water Absorption of Plastics

This investigation is based on ASTM D-570, the Standard Test Method for Water Absorption of Plastics. Water absorption, as previously discussed, is a negative attribute which requires processors to dry plastics before molding. This investigation will look at water absorption as a positive attribute in a different application.

1. Dry polyacrylamide overnight in a 50 °C oven.
2. Place an empty freezer bag on the balance and record mass to 0.001 g.
3. Transfer 2–3 cm^3 of dried polyacrylamide to the baggy and weigh to 0.001 g. Subtract the mass of the empty bag, then record the mass of the crystals as the dry mass.
4. Add distilled water until the material will not absorb any more.
5. Drain any excess water, remass the bag and calculate the mass of the water logged material as the wet mass.
6. Calculate the amount of water absorbed and the percent increase in mass as follows:

$$\text{wet mass} - \text{dry mass} = \text{mass of water in grams}$$

$$\frac{\textit{wet mass} - \textit{dry mass}}{\textit{dry mass}} \times 100 = \%\ \textit{increase in mass}$$

7. Carefully transfer all the polyacrylamide into a foil pan and dry in a 50 °C oven for 24 hours.

8. Cool in a dessicator 10–15 minutes and weigh the redried material.
9. Determine if anything dissolved out of your remaining sample as follows:

$$\frac{\textit{dry mass} - \textit{redried mass}}{\textit{dry mass}} \times 100 = \textit{\% soluble material lost}$$

* If the redried mass is larger than the original dry mass, return the material to the oven to drive off the remaining water. This can be done by heating, cooling, and weighing until the mass remains constant.

10. Calculate the percent water absorbed by adding the percent increase in mass and the soluble matter lost.

Questions

Investigation #1

1. Draw the repeat unit for the polymer used in this investigation.
2. Compare your results to the atomic composition of your polymer or to known standards for your material. Discuss whether or not the hydrophobic and hygroscopic tendencies were proven to be true. If not, what could be a possible conclusion?
3. Compare your data to class results and, if possible, to known data. Were the class results uniform? Determine averages and standard deviations. Discuss the results in terms of accuracy and precision.
4. (optional) Did the extended soaking time change the results?
5. Explain how the %-crystallinity of polyethylene or polypropylene affects the absorption of water or the transmission of water vapor through the film.
6. Give examples of end-use applications where polymers with intrinsic moisture barriers are important and examples where absorption of water is important.

Investigation #2

7. Explain how this investigation confirms the hydrophobic and hygroscopic nature of plastics based on their atomic composition. If not, what explanation could you give for the inconsistency?

Investigation #3

8. Create a data chart for your data.
9. Describe what occurred.
10. Compare your results to other students' results. Discuss possible sources of any variations.

References

1986 Annual Book of American Society for Testing and Materials, Volume 8.01 "D-570 Standard Test Method for Water Absorption of Plastics"; ASTM: Philadelphia, PA, 1986; pp. 532-533.

Richardson, T. *Industrial Plastics: Theory and Application;* Delmar Publishing, Inc.: New York, 1986.

Shah, V. *Handbook of Plastics Testing Technology;* John Wiley & Sons: New York, 1984.

III. INSTRUCTOR NOTES

Water and Polymers

Purpose

These activities represent both qualitative and quantitative investigations based on the interaction between water and various polymers. The first two activities will determine the inherent moisture present in plastic samples which effect the molding and physical properties of plastics. The third investigation will have students determining the percent moisture absorbed by a hygroscopic crosslinked polymer. All of these activities are based on hydrogen bonding of water to plastics.

Time Required

Investigation #1 will take two 50 minute class periods or one 2 hour lab period. Investigation #2 will take one 50 minute class period. Investigation #3 will take place over 3 days and depends, as do #1 and #2, on the number of balances and hot plates that are available.

Suggested Group Size

This can be done by any size class although the number of balances and hot plates available may dictate that students work in small groups.

Materials Needed

Per class

- oven(s) (Drying ovens are preferred here.)
- heat resistant gloves
- analytical balances (accurate to 1 mg)

Per group

<u>Investigation #1</u>

- 1–2 grams plastic pellets (1-2 grams per student for both Investigations #1 & #2. These can be obtained from any plastics processing company or compounder. Ask for the name of each sample and the chemical formula, also whether it contains any additives. Or order from Aldrich Chemical Company; 1-800-558-9160. Interesting comparisons can be done between the results in Investigation #1 and #2 when the same pellets are used. Polystyrene is recommended.)
- foil pans or glass 50-mL beakers (1 for each sample)
- desiccator
- (optional) hot water

<u>Investigation #2</u>

- various plastic pellets (see comment above)
- 2 glass microscope slides per sample (heat tempered)
- hot plate
- wooden tongue depressor
- (optional but very useful) magnifying glass
- tongs

Investigation #3

- polyacrylamide crystals (Can be obtained from garden stores as "Soil Moist" or from Flinn Scientific as "Ghost Crystals." Flinn Scientific can be reached at 1-800-452-1261.)
- distilled water
- sandwich size ziptop freezer bags
- foil 8–9 inch cake pans
- dessicator

Safety, Handling, and Disposal

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

- Be careful when handling hot materials in the oven or on hot plates.
- Use heat resistant gloves or tongs as indicated.
- Use a tongue depressor to sandwich the plastic to avoid burns when completing the TVI test.

Points to Cover in Pre-Lab

- Draw the structure for the repeat unit.
- Students should be able to identify the elemental composition of the polymers they are testing and hypothesize expected results.
- Review analytical measurements and use of analytical balances.
- Discuss the statistical treatment of data and sources of error.
- Discuss how to search the literature and Internet for data.
- Introduce or review Van der Waals forces, dipole-dipole interaction, and hydrogen bonding.
- Review types of bonding and intermolecular attractions (above) and their relative strengths.
- Discuss how molecular structure and charge distributions affect properties (melting point, boiling point, solubility). The physical and chemical properties of molecules can be understood based on an understanding of the charge distribution among the atoms. This results in electrostatic forces which range from strong ionic bonds (e.g., $Na^+ Cl^-$) to weak van der Waals interactions between nonpolar neutral molecules (e.g., propane). The order of decreasing electrostatic forces is:

ion-ion >> ion-dipole > dipole-dipole > dipole-van der Waals >> van der Waals-van der Waals.

In general "like dissolves like" and the greater the strength of the attractive forces, the greater the melting and boiling points.

- Hot plates and heated slides can cause serious burns. Remind the students to always use tongs or heat resistant gloves when handling hot items.
- Remind students to use only distilled (or deionized) water in Investigation #3.

Procedural Notes and Suggestions

- If using 100 °C oven, use heat resistant gloves to avoid burns when putting in and taking out samples.
- In Investigation #2, each material will melt at a different rate. It is strongly suggested that you practice your technique and choose pellets that melt readily without bubbling or scorching.
- Investigation #3 is a good investigation if you have a limited number of analytical balances. Polyacrylamide can also be replaced with pellets used in the first two activities to find the saturation point of the materials already tested.

- Be patient with the polyacrylamide. It may take a while (20–30 minutes) to swell. To become saturated, you may need to leave the polyacrylamide in excess water overnight. Using warm water will also hasten the process.
- In Step 6 of Investigation #3, check to be sure that students subtract the mass of the empty bag before calculating the %-increase in mass.
- In Step 7 of Investigation #3, the redried polyacrylamide should mass the same as or less than the original dried mass. If the redried polyacrylamide is found to weigh more than the original dried mass, have the students return it to the oven and continue the drying, cooling, weighing process until a constant mass is obtained.

Sample Results

Activity #1: The following are reasonable 24 hour water absorption values.

Material	Percent Moisture
ABS (acrylonitrile-butadiene-styrene terpolmer)	0.20–0.45
Acetals (formaldehyde polymers)	0.22–0.25
Acrylics (e.g. polymethylmethacrylate)	0.30–0.40
Cellulose acetate	2.00–7.00
FEP (fluorinated ethylene propylene)	0.01
Nylon 6	1.30–1.90
Nylon 6–6	1.50–2.00
Nylon 6–10	0.40
Polycarbonate	0.15–0.35
Polyester (PETE)	0.38–0.80
Polyethylene (LDPE, HDPE)	0.010
Polypropylene	0.010
Polystyrene	0.03–0.60
PTFE (polytetrafluoroethylene)	0.010
PVC (rigid to flexible)	0.07–0.75

Tests performed on polystyrene (3/98) gave an average value of 0.032%.

Activity #2: Tests (3/98) on similar sized samples of polystyrene and polyethylene terephthalate (PETE) resulted in 58 bubbles and 98 bubbles respectively.

Activity #3: Test (3/98) resulted in an approximate 1000% (10 fold) increase in wet mass.

Plausible Answers to Questions

Investigation #1

1. Draw the repeat unit for the polymer used in this investigation.

A: This will depend on the polymer(s) provided.

2. Compare your results to the atomic composition of your polymers or to known standards for your material.

A: Modern Plastics Encyclopedia or the company provided physical data charts are a good source for this information. Request a data sheet when you acquire your plastic samples. The Handbook of Plastics Testing and Technology is also an excellent general source of information.

Discuss if the hydrophobic and hygroscopic tendencies proved true. If not, what could be a possible conclusion?

A: Virgin uncompounded materials should react true to form. C, H and C, H, halogen polymers could have %-moisture values less than 0.001 but, as indicated on the chart, can be greater than 0.01%. Those polymers with O, N, or additives can have up to 7% moisture. Certain thermoplastic elastomers (such as some olefins) will have up to 50% moisture in extremely humid conditions. If student data does not follow the expected trends, a discussion of technique and sources error would be appropriate. Some materials are very water sensitive and will absorb water very rapidly. Samples that are left out of the dessicator even 10–15 minutes can begin to absorb water. Younger students are not generally as careful in their technique and are not familiar with taking measurements accurate to 1 mg.

3. Compare your data to class results and, if possible, to known data. Were the class results uniform? Determine averages and standard deviations. Discuss the results in terms of accuracy and precision.

A: This lab is highly sensitive to lab technique. Class results should be both accurate and precise relative to known data. (Known data can be found in testing texts, the Modern Plastics Encyclopedia, and literature from the manufacturer.) Students generally have not experienced tremendous accuracy or precision in measurement in prior lab work. This investigation provides an opportunity to improve those skills.

4. (optional) Did the extended soaking time change the results?

A: Some plastics would not show any difference in %-moisture since they are hydrophobic and reach their saturation point when exposed to ambient conditions. Other materials would have an increased %-moisture but may not reach saturation unless left to soak in water for extended periods of time. Investigation #3 looks at water absorption characteristics of plastics.

5. Explain how the %-crystallinity of polyethylene or polypropylene affects the absorption of water or the transmission of water vapor through the film.

A: The Moisture Vapour Transmission Rate (MVTR) is an important property of materials used for food packaging. Since small molecules must migrate through the amorphous regions of the material, the higher the crystallinity, the more difficult that becomes and the less that can be absorbed. Also, in higher density (crystallinity) materials the small molecules would have to follow a much more tortuous path thus lowering the MVTR. In some applications of, for example, polypropylene (PP), a non-compatible high density polyethylene (HDPE) is added which will crystallize in the amorphous regions and further improve the barrier properties.

6. Give examples of end-use applications where polymers with intrinsic moisture barriers are important and examples where absorption of water is important.

A: In most packaging applications (food, drugs, etc.), it is important to exclude moisture. Most plastic food containers have multilayer polymers. On the other hand, the sodium polyacrylate used in disposable diapers is an example of where the absorption of water (urine) is important. The water solubility of polyvinyl alcohol makes it useful for hospital laundry bags and pesticide and herbicide containers.

Investigation #2

7. Explain how this investigation confirms the hydrophobic and hygroscopic nature of plastics based on their atomic composition. If not, what explanation could you give for the inconsistency?

A: This should be consistent with the hydrophobic and hygroscopic nature of materials. The most common error is to over-heat pellets causing boiling. In this case the bubbles are trapped gas not water. Technique can cause inconsistencies.

Investigation #3

8. Create a data chart for your data.

A: These will vary with each student.

9. Describe what occurred.

A: Polyacrylamide is a crosslinked material of polyacrylamide and bis-acrylamide. As the water hydrogen bonds to the unshared electrons of the nitrogen and oxygen of the polyacrylamide, the polymer structure begins to unfold exposing more nitrogen and oxygen. Using a fish net, you can visually demonstrate the unfolding process. When the material is dried, the water evaporates and the material returns to its compact state. It is good to note to students that this was not a chemical reaction. If students had a soluble matter loss greater than zero they need to explain this. They could have washed off oils and dirt, something dissolved out, particles were lost in transfer, or their technique was faulty.

10. Compare your results to those of other students. Discuss possible sources of any variations.

B: Techniques will cause tremendous variations in results. If students use the same techniques, results should be very close unless there were differences in the temperature of the water used. If some students used tap water and others used distilled water there could also be variations.

Extensions and Variations

1. Using this procedure, the saturation point of the polyacrylamide can be determined. Using the polyacrylamide, take a dry mass of É teaspoon. Then immerse in distilled water for 24 hours, drain and take a wet mass. Return to the water and repeat the massing after 48 hours, 1 week, 2 weeks, etc. Determine the saturation point of the crystals. How much water was absorbed compared to the original dry mass of the polyacrylamide? Note also that the index of refraction of water and the polyacrylamide crystals is the same. Don't worry if it seems as if your crystals disappear in the water. Repeat the above experiment using 1–2 grams of plastic pellets. Use an analytical balance and mass to 0.001 g for all masses. In this case

soluble matter lost could be additives that are dissolved out. Take wet masses at 24 hours, 48 hours, 1 week, 2 weeks, etc. Then redry the pellets. Investigate the hydrophobic and hygroscopic nature of various pellets, or of uncompounded plastics compared to compounded plastics.

2. Polyacrylamide can be used very well as an observational skills investigation in a constructivist format. Place a teaspoon of dried crystals in a freezer baggy, preferable non-pigmented. The students are then asked to work alone or in small groups to answer the following questions. Answers can be recorded and/or shared during a class discussion.

a. Describe the contents of the bag including size, shape, color, & weight.
   What do you think it is?
   What is your reasoning for this choice?
   What do you think will happen if you add water?
   At this point if students have not seen this material before they will assume it is rock salt which will dissolve, rocks which will sink in water, or some very creative substance. The idea is to look at logic and the completeness of their descriptions.
b. Add approximately 200 mL of water. Describe what you observe happening over the next 10 minutes.
   Use room temperature water for students to measure the endothermic reaction or very warm water to speed of the process.
c. From your observations, what do you think has occurred? Explain your reasoning.
d. Was your identification of the material accurate? Explain why or why not.
   Still without any information from the teacher, the students analyze their first assumptions.
e. What would be 3 or 4 appropriate applications for this material? Explain your choices.
f. What do you think will happen if you dried this material? Explain. Dry the material over night.
g. Describe the material after drying.

The following questions can be used as a follow up to this investigation. Before students begin, discuss the material and explain what has happened. It is important to dispel erroneous information and misconceptions while validating the investigative process they used.

1. Explain why observation is or is not always correct.
2. Describe why observation is a skill that can be developed.
3. List several items which will affect someone's observational skills.
4. In our observational activity, how could bias affect observations and reporting? What bias did you bring to the activity?
5. What portion of the activity was interpretation? What will affect your interpretation of an investigation?
6. Discuss how using the scientific method might help to eliminate some of the problems you bring up above.
7. Using one of your suggested applications of the material in the bag, outline how you would test to see if the material is suited to the application you suggest.

References

1986 Annual Book of American Society for Testing and Materials, Volume 8.01 "D-570 Standard Test Method for Water Absorption of Plastics"; ASTM: Philadelphia, PA, 1986; pp. 532-533.

Richardson, T. *Industrial Plastics: Theory and Application;* Delmar Publishing, Inc.: New York, 1986.

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