To close the yellow note, click once to select it and then click the box in the upper left corner.
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#1 Examination of the Degradation and Weathering of Polymeric Materials

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I. INTRODUCTION

Description

This lab investigates issues of degradation and weathering of polymeric materials during their useful life. The first activity will look at the qualitative changes in film materials when exposed to weathering. This activity will also have students evaluate photodegradable plastics and their viability as an environmental solution for litter. The second activity will have students investigate the qualitative changes in other polymer products when exposed to weather.

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:

- analyze materials at the macroscopic level and extrapolate to the molecular level,
- develop and improve observation skills,
- record long-term data and potentially develop charts to organize the data,
- investigate the effects of moisture on different polymeric materials,
- relate weather data to qualitative changes of materials tested, and
- relate data to service life of products.

Recommended Placement in the Curriculum

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

- environmental chemistry,
- science, technology, and society,
- materials science,
- molecular structure,
- intra- and inter-molecular attractions,
- polymers, and
- meteorology.

STUDENT HANDOUT

Examination of the Degradation and Weathering of Polymeric Materials

Scenario

Weed-Not is a company which manufactures mulch film for farmers. Recently the number of complaints received about this product has increased dramatically. According to farmers using the polymer mulch, it is degrading much too rapidly during use and thus not lasting a single growing season. Investigation shows that the vast majority of the complaints involve lots of film produced in November of last year.

The Weed-Not Quality Control lab is investigating this problem from several different perspectives. For example, one technician is determining the concentration of UV inhibitor in both the raw materials and in the extruded film. (UV inhibitors increase the product stability by interfering with the degradation which normally occurs when the film is exposed to UV light.) One of the reasons for the rapid degradation may be the destruction of the UV inhibitor during production due to the extruder being too hot. Or, the raw materials from the polymer supplier may not contain the amount of inhibitor specified in the Certificate of Analysis issued by the resin supplier.

Your job as another chemical technician for Weed-Not is to field test quality control samples of the mulch film from the complaint lots. These tests will limit the factors other than exposure to UV light and other weather conditions. That is, pesticides and other materials the farmers might put on their fields will not be considered. Thus, if the field testing shows the rapid degradation experienced by the farmers, the source of the problem will be narrowed down.

Industrial Application

Aging of polymeric materials is a critical issue for materials used in outdoor applications. House siding, paint, garden hoses, sealants, and patio furniture are only a few of the myriad of products whose exposure to weathering may cut short their service life. Weather not only leads to increased maintenance costs but also to the inconvenience of having the material repaired or replaced and to potential safety hazards.

This investigation will focus on the process of weathering materials as well as the interpretation of the results. Weathering is caused predominantly by light, heat, and moisture with exposure to oxygen, ozone, and various pollutants also contributing to the aging of polymers. Light or heat can cause the polymeric materials to become more crystalline with age. For example, the heating and cooling of the weathered material causes the molecular chains to rearrange, becoming more closely packed with each cycle. UV radiation promotes the formation of free radicals, which in turn can act to shorten polymer chains and increase crosslinking.

These changes at the molecular level are reflected in changes in physical properties, such as loss of clarity, or changes in impact and tensile strengths. Clarity is a measure of the transparency or freedom from haze of polymer film as determined by ASTM D 1003. Impact strength is the ability of a material to withstand shock as determined by any of several ASTM test methods. Tensile strength is the pulling stress, in pounds per square inch, required to break a given specimen. The area used in computing tensile strength is the original area rather than the necked down area. Moisture will affect materials with molecular structures containing oxygen and/or nitrogen, as well as materials which contain fillers, pigments, or plasticizers. Moisture can result in hygroscopic materials absorbing water, resulting in changes of physical and mechanical properties, or soluble additives leaching from the sample. UV inhibitors, antioxidants, and antiozonants are some of the additives that help protect polymeric materials from aging.

Investigation #1

The first activity will look at film materials which may or may not include a photodegradable additive which is designed to help materials degrade when exposed to light. This type of additive has become popular as a means of combating litter and other environmental concerns. In this investigation, you will investigate the effects of weathering on film samples. The samples will be evaluated by visual changes and by the difference in qualitative tensile strength between exposed and unexposed samples over an extended period of time. As the materials age, the photodegradable additive absorbs radiation, which will weaken intramolecular bonding and intermolecular attractions and cause the polymer network to break into smaller segments. The materials should therefore produce lower tensile test results over time. By cutting samples both with and against the direction of extrusion, it is possible to determine whether intramolecular bonding or intermolecular attractions are affected first. Note that the direction of extrusion is determined by the extrusion process of applying heat and pressure to melt a resin and forcing it continuously through a die of the shape required for the finished product. The samples may be anisotropic; that is, they may have different physical properties when measured parallel and perpendicular to the direction of extrusion. Since most of the film materials used in these applications are polyethylene, which is hydrophobic, we will not consider the moisture factor of weathering.

Investigation #2

This activity will look at weather resistance of rigid polymeric material samples, preferably obtained from products which are used outdoors during their service life, such as paint samples, children’s toys, vinyl siding, or garden hose. Materials will be assessed not only qualitatively for visual changes (color change, surface conditions, cracking, crazing, spotting, bleeding), but also quantitatively for effects of moisture.

Safety, Handling, and Disposal

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

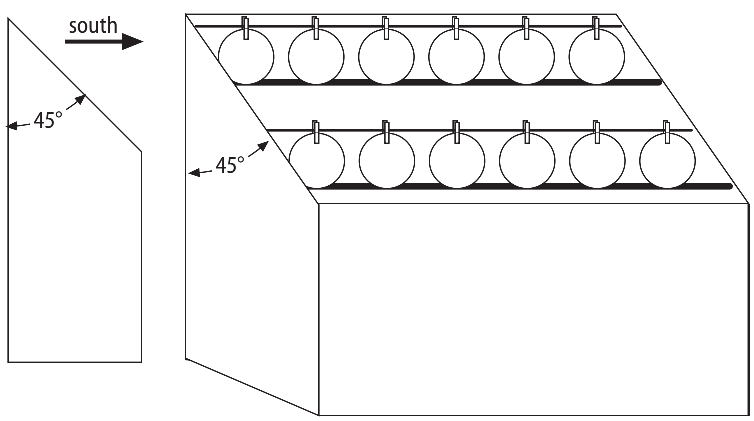
Materials

Investigation #1

- scissors
- 3-inch embroidery hoop for each sample
- clothespins (spring opening)
- permanent markers
- rack with southern exposure to hang hoops and tensile bars (See Figure 1 for suggested design.)
- hooks or wire to hang hoops on rack
- various samples of plastic film (e.g., trash bags, window insulation, mulch film, six-pack can carrier)
- (optional) polyurethane wood preservative for hoops

Investigation #2

- scissors or tin snips
- clothespins (spring opening)
- rack with southern exposure to hang the samples (See Figure 1 for suggested design.)
- wire to hang samples on rack
- drill with ¼-inch bit
- various samples of plastic (e.g., siding, garden hose, house paint)



Procedure

Investigation #1

1. (optional) Coat the wooden embroidery hoops with polyurethane wood preservative to weatherproof them and allow them to dry completely before use.
2. Cut a film sample at least 4 inches x 4 inches so to fit securely in a 3-inch embroidery hoop. One sample should be prepared for each week the test will progress. Repeat for each of the various film samples being tested.

3. Cut a control sample for each material and place it in a dark closet, drawer, or an opaque bag for the duration of the experiment.
4. Clamp each of the film samples into a hoop so there are no creases or tears in the sample.
5. Using the template for the tensile bar (see Figure 2, attached), cut one tensile bar for each week of the proposed test both with and against the direction of extrusion of the sample film. (The direction of extrusion is usually evident when the sample is held up to a light. The grain of the sample corresponds to the direction of extrusion and is often visible as striations, streaks, or lines parallel to that direction.) Also cut an equal number of tensile bars to be kept as controls. The tensile bars should be cut with the length of the sample parallel to the direction of extrusion and a second set perpendicular to the direction of extrusion to determine the anisotropic nature of the material. Label each sample with the name and extrusion direction.
6. Hang samples on a rack so they face the southern exposure and, if possible, tilt at a 45° angle. Nothing should cast a shadow on the samples during the test period. Record the date and time when the samples are put outside. Tensile bars can be attached to the weathering rack using the clothespins.
7. Keep a daily record of the sunrise, sunset, precipitation (amount and kind), high and low temperatures, and the Pollution Standard Index (PSI) from the newspaper, TV, radio, or local weather service. (Sample chart follows.) A weather station is good for obtaining not only simple data but percent radiance information. University geology/meteorology departments may have a station on site that can be used to obtain needed information. Or there may be an Internet site which reports weather information for your area.
8. Each week compare samples to the control. Calculate the approximate number of hours of light using the sunrise and sunset data, total hours of exposure, average high temperature, average low temperature, and the mean temperature. Analyze the resulting data, comparing the control to exposed samples in terms of degradation, disposal, service use, and the environment.
9. Test the tensile strength for each sample (exposed and unexposed samples both with and against the grain). Begin with the control sample in each case and then test the corresponding weathered sample. Grip the ends of the tensile bar and pull slowly to moderately. (All samples should be pulled at approximately the same rate.) Stress is being applied, causing a strain which can be felt. Continue to pull until the tensile bar breaks.
10. Compare the tensile tests of exposed and unexposed samples both with and against the grain. Determine if greater degradation has occurred with the intramolecular bonds (that is, in the direction of extrusion) or with the intermolecular attractions (that is, perpendicular to the direction of extrusion).
11. Continue the experiment for a minimum of one month or until samples have degraded completely.

Investigation #2

1. Prepare samples by cutting 4-inch by 6-inch samples of flat materials or 4-inch to 6-inch lengths of tubing. Cut one sample for each week of the test for each material being tested. Drill a ¼-inch hole in the top and bottom of the sample for attaching to the weather rack.
2. Prepare a control sample of each material and place it in a charged desiccator in a dark closet or an opaque bag for the duration of the experiment after conditioning.
3. Use a permanent marker to mark the sample number on the back side of each sample. Condition all samples in a drying oven for 24 hours at 50°C. Remove samples and take an initial mass for each sample to ±0.001 g.
4. Hang samples on a rack so they face the south and preferably are tilted at a 45° angle. Nothing should cast a shadow on the samples during the test period. Record the date and time when the samples are put outside.
5. Keep a daily record of the sunrise, sunset, precipitation (amount and kind), high and low temperature, and the Pollution Standard Index (PSI) from the newspaper, TV, radio, or local weather service. (Sample chart follows.) A weather station is good for obtaining not only simple data but percent radiance information. University geology/meteorology departments may have a station on site that can be used to obtain needed information. Or there may be an Internet site which reports weather information for your area.
6. Each week, calculate the approximate number of hours of light using the sunrise and sunset data, total hours of exposure, average high temperature, average low temperature, and the mean temperature. Analyze the resulting data, comparing the control to exposed samples in terms of degradation, disposal, service use, and the environment.
7. After making visual observations, wash and dry the sample to remove pollen and dust. Take a final mass for each sample and calculate the percent change in mass of the sample. The percent increase in mass represents the water absorbed into the sample from exposure.

$$\frac{\text{mass (f)} - \text{mass (o)}}{\text{mass (o)}} \times 100 = \text{\% percent increase in moisture}$$

8. Continue the experiment for a minimum of one month or until samples have degraded completely.

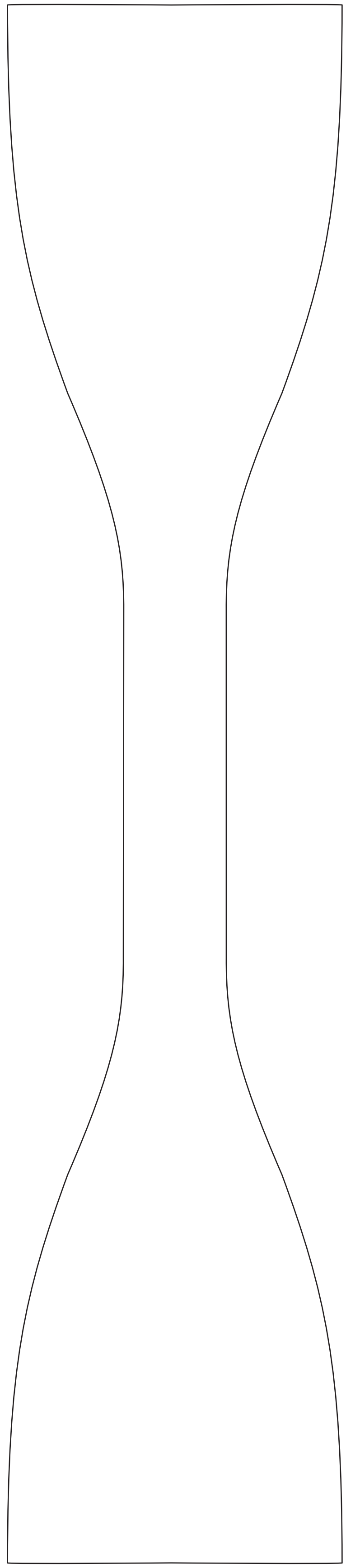
Outdoor Weather and Degradation Chart

Outdoor Weather and Degradation							
Day							
Date							
Sunrise (start)							
Sunset							
High Temperature (° F)							
Low Temperature (° F)							
Pollution Standard Index							
Precipitation type							
Precipitation amount							

Questions

1. Discuss whether or not UV-degradable films will help to solve the litter problem in our country.
2. Based on your observations, how does the direction of extrusion affect tensile testing? Do the films tear more easily in one direction than in the other? Explain in terms of chain alignment.
3. Give examples of where this anisotropy (having differing properties depending on the direction of measurement) in physical properties is advantageous.
4. Describe where weathering is first evident in film samples.
5. Describe the difference in results of weathering of virgin uncompounded materials and those that have been processed/compounded.
6. Since weathering is a long-term process, how would you devise an apparatus to accelerated the effects of aging?

Figure 2 Tensile Bar Template



III. INSTRUCTOR NOTES
Examination of the Degradation and Weathering of Polymeric Materials

Purpose

These activities will investigate the effects of weather on polymeric materials and how the results impact actual use of the materials. Both activities are examples of long-term investigations in which daily data is collected. Analysis of the data compared to a control sample is done on a weekly basis.

Time Required

Initial sample preparation will require approximately one 50-minute class period provided all materials are set up and ready to go (e.g. hoops, scissors, samples, rack, tensile pattern). Minimal daily time is needed for data collection and can be done outside of class.

You may want to post daily weather data which students record at their leisure. If computer generated data from a weather service is available, the data may already include average temperatures, total rain fall, etc. which will eliminate the need for students to do this. If this is the case they will only be observing samples and not calculating data. This is a time saving device, but for many students the data calculations prove to be a weak skill, and you may want to recommend that the students use calculators or computers to generate this information from raw data.

The total length of the project should be at least four weeks, but the longer the project goes on the better, as some materials take up to three months to degrade. This could be done as a semester project.

Each stage of analysis will take at least one 50-minute class period. The length of time will depend on the number of different materials each student tests and whether they are collating raw data or not.

Suggested Group Size

This is an excellent cooperative education activity for students to work in teams of 3-4. The groups can look at several materials, or each team can do a different material and then present the results to the class. The availability of space for hanging samples may determine the number of samples that can be tested at one time. Then class analysis can be done of the different materials' results, or analysis of the replicated data can be done.

Materials

<u>Investigation #1</u>

- scissors
- 3-inch embroidery hoop for each sample
- clothespins (spring opening)
- permanent markers
- rack with southern exposure to hang hoops and tensile bars *(It is suggested that the construc-*

tion of a weathering rack be done as a separate project by chemistry, industrial trade, or engineering students according to the ASTM D1435. If this is not feasible, a simple clothes-line set up can be used instead. You may prefer that the students design their rack outside of class and bring it to the first lab period. If space is limited window ledge racks can be designed. The most important factors are that the rack holds samples at a 45° angle and that they face the southern exposure.)

- hooks or wire to hang hoops on rack
- various samples of plastic film (trash bags, window insulation, mulch film, "green" trash bags, six-pack can carrier)
  - (optional) polyurethane wood preservative for hoops *(This should be done several days to weeks prior to the lab so the coating cures and dries.)*
- data charts *(Sample chart follows.)*

Investigation #2

- scissors or tin snips
- clothespins (spring opening)
- rack with southern exposure to hang the samples (See diagram for suggested design.)
- wire to hang samples on rack
- drill with ¼-inch bit
- various samples of plastic (e.g., siding, garden hose, house paint)

Safety, Handling, and Disposal

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

Points to Cover in Pre-Lab

This will vary with the intended use and placement in curriculum by each teacher.

- Be specific about goals.
- Have students discuss issues regarding various types of pollution and the environment.
- Discuss service life of products. Generally, students are very vague in their descriptions and will need to be taught how to analyze service life of a product.
- Discuss economics in relation to longevity.
- In use and product development, the physical and mechanical properties are important for the function of products. At the same time, aesthetics (e.g., color, surface texture) are equally important to the consumer and will often be as important as function.
- Discuss the variables of weather. Check references or earth science texts for further information on weather, climate, and location.
- Discuss the vocabulary in this lab that may be new to students (e.g., anisotropy, direction of extrusion, etc.).
- Discuss possible modes of degradation, such as chain scission, oxidation, cross-linking, photodegradation, and/or biodegradation. For example, photodegradation results from the action of natural sunlight. The effect of UV radiation is seen with the "yellowing" of synthetic garments. The preferred theory for the mechanism begins with the formation of free radicals. The reactions of these free radicals are dependent on the specific material involved and the physical state of the material.

- Consider including outside student research over the length of the lab. Have students investigate topics related to this project in terms of the chemistry involved, the industrial point-of-view, and customer satisfaction.

Procedural Tips and Suggestions

Some general procedural suggestions include:

- Remind students to keep a control sample. This is often forgotten and then the data is not useful since our interest is in the changes that occur.
- Labeling needs to be done with permanent markers and on the reverse side of samples since the student is not investigating the changes in the ink.
- Clear samples should be marked with tags or on excess film that extends past the hoop.
- Do not use photodegradable fishing line to tie samples in place in Investigation #2.
- Choose a variety of samples including a film sample that will degrade in the light. “Green” or environmentally safe trash bags can be used although most trash bags now have photodegradable additive in them. You will see more degradation in these samples. Other packaging plastics, such as potato chip bags, sandwich bags, and cookie wrappers do not generally have photodegradable additive in them and will not be as affected by weathering.
- A weather station is good for obtaining not only simple data but percent radiance information. University geology/meteorology departments may have a station on site that can be used to obtain needed information. Or there may be an Internet site which reports weather information for your area.
- Students will need to have direction in noticing changes that occur. Usually, younger students’ observation skills are weak, and they will need assistance to develop and hone these skills.
- Calculating hours of light and dark may seem simple, but this often is a difficult task for students. Be prepared to walk them through these calculations. Hours of light are calculated by determining the hours between sunrise and sunset. Dark hours are calculated from sunset to sunrise or total test hours minus light hours. This is estimated data but the availability of more definitive data at each test site is cost prohibitive for general classroom use if not highly improbable to obtain.
- As the material weathers, the strain will likely lessen as the material weakens. Students will note the samples pulled perpendicular to the anisotropy will likely weaken first, indicating the degradation of intermolecular attractions.
- This is an important qualitative observation that students would not experience with a tensometer. Seeing variations in numbers has its place in quantitative analysis but the visual and tactile differences often seem more “real” to students. If you wish to use a more quantitative test here, refer to the laboratory investigation entitled “Simple Tensile Testing of Polymeric Films and Sheeting.”

SAMPLE RESULTS

Outdoor Weather and Degradation Chart

Outdoor Weather and Degradation							
Day	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday
Date	5/13	5/14	5/15	5/16	5/17	5/18	5/19*
Sunrise (start)	9:50 AM	6:09	6:08	6:07	6:07	6:06	6:05
Sunset	8:34 PM	8:35	8:36	8:37	8:38	8:37	8:38
High Temperature (° F)	64	62	54	55	63	81	79
Low Temperature (° F)	40	42	41	40	45	44	60
Pollution Standard Index	44	42	38	34	NA	NA	54
Precipitation type	rain	rain	rain	rain	rain	rain	rain
Precipitation amount (inches)	trace	0.02	0.01	0.04	0.01	0.59	0.18**

(Reminder: Do not use high, low, PSI etc. for weekly average since the sample was removed in the early morning and was not exposed to those conditions. If the samples were exposed to rain, it is easier to remove samples when there has not been rain from midnight to the time a sample is removed.)

Observations: After 1 week, the surface of the sample appeared to have become dulled compared to the control. The grain of the material is slightly more prominent in the aged sample than the control. There is no change in color or texture, and tensile results seem to be no different between the aged sample and the controls either with the anisotropy or against (that is, either in the machine direction or perpendicular to it).

Plausible Answers to Questions

1. Discuss whether or not UV-degradable films will help to solve the litter problem in our country.

   A: Not all plastic films are UV-degradable, therefore improperly disposed of films remain an issue. Secondly, the average photodegradable film takes a minimum of a month to degrade (if not significantly longer) so the effects to the environment still exist for an extended period of time. Most areas of our country dispose of trash in landfills, and the trash is buried before it has time to degrade. This is also true for biodegradable films since most landfills are anaerobic, and these films generally require aerobic conditions to degrade.

2. Based on your observations, how does the direction of extrusion affect tensile testing? Do the films tear more easily in one direction than in the other? Explain in terms of chain alignment.

   A: As a film is extruded or blown, the molecules in the plastic tend to orient in this direction, therefore a tensile bar pulled with the direction of extrusion will be stretching the polymer chains and breaking the covalent bonds of the molecules. The tensile bars cut and pulled perpendicular to the direction of extrusion will result in the stress being put on the intermolecular attractions. This will be seen more readily if the tensile bar is pulled quickly, effectively not giving the molecules an opportunity to reorient as indicated by necking that occurs when the tensile bar is pulled. Note that the tensile testing results will also depend on the specific material being tested and on its density. This makes the control samples particularly important.

3. Give examples of where this anisotropy (having differing properties depending on the direction of measurement) in physical properties is advantageous.

   A: Generally polymer chains tend to align in the extrusion direction also called the machine direction (MD), and this preferred orientation causes anisotropic properties. There are many applications where highly oriented polymer chains are desirable. These include fibers (nylon, polyester, etc. for textiles, tire chords, carpets, Kevlar, HDPE sails) and ropes (nylon, fishing nets). Most grocery bags and garbage bags are oriented and cut in such a way to increase the load bearing strength. It is also desirable to be able to tear open some plastic packaging in one direction but have strength in the other. Extruded PP and HDPE rods as replacement for wood in building materials tend to be unidirectional.

   Some new up-and-coming materials that involve induced alignment of polymer chains are special liquid crystals for energy efficient displays and various electro-optic devices. Polymer-dispersed liquid crystals where the liquid crystal molecules change orientation with an electric field and vary the intensity of transmitted light show promise for applications ranging from switchable windows to projection displays.

4. Describe where weathering is first evident in film samples.

   A: Generally, you will first see degradation along the lines of extrusion. This means that the intermolecular attractions will weaken first and students will see weakness and cracks along the direction of extrusion, between the molecular chains. Materials which are plasticized, PVC and PVDC for example, will also show bleeding of plasticizer. Different types of polymers, such as olefins, are more inherently resistant to weathering. Others will show a change in color that could be from weathering effects on pigment or the plastic.

5. Describe the difference in results of weathering of virgin uncompounded materials and those that have been processed/compounded. (Note, students will only be able to answer this if virgin/uncompounded material are included in the samples. Suppliers can be found in the Thomas Register and in plastics trade journals such as *Modern Plastics* or *Plastics News.*)

   A: Weathering of uncompounded material will let the investigator see the effects of aging on the polymeric material alone, such as breakdown of intermolecular attractions, increase in crystallinity, or color change due to crystallinity or degradation. Compounded materials are more complex since they may contain a myriad of possible other chemical compounds which will also be affected by weathering. Changes seen could be the result of such things as a plasticizer bleeding from the plastic, pigment reacting to UV, or temperature masking the changes or lack of changes in the polymer being studied.

6. Since weathering is a long-term process, how would you devise an apparatus to accelerated the effects of aging?

   A: Since the main factors affecting aging are light, heat, and moisture, a devise can be designed to age plastics in an accelerated manner. The disadvantage of this is that, even in industrial Xenon Arc or QUV testing, there is not a defined correlation between accelerated aging and natural weathering. Still the effects of weather can be determined in a much more timely basis. ASTM G-53 is an example of accelerated weathering that can be used as a model. This process allows students to break down the process of weathering to devise a method of testing that increases the intensity of the UV and moisture in the form of condensation. Since condensation is pure water, spotting on aged samples can then be attributed to bleeding from the polymer rather than water spots.

Extensions and Variations

1. For a more constructivist approach to Investigation #1 the teacher may present the dilemma of plastic litter and its effects on the environment. Have the students research and discuss this particular environmental issue and the possible solutions they found or can suggest. During the class, offer the solution of photodegradable materials, showing “Green” plastic trash bags, six-pack rings, and fishing line as some examples of products made with photodegradable additives. Have students read ASTM D-1435 and G-53 and design an investigation to see if photodegradable additives are a viable solution to this litter problem.

2. Likewise for Investigation #2, students can visit a discount store or peruse a sale advertisement for the variety of polymeric products which must withstand weathering during their service life. Have students pick a product and describe the service conditions it will go through during it service life (e.g., rain, cold, and light). Next the student can be asked to determine what detrimental effects may result if the product cannot withstand being exposed to weather (e.g., fading, surface changes, cracks, loss of physical or mechanical properties). Again, have students read ASTM D-1435 and G-53 and design an investigation to see the effects of weathering on their product. An analysis of aging results to service expectations can be produced.

3. Investigations can be made to include the studies of the effects of acid rain. Students prepare sulfuric or nitric acid solutions with pH of 3 and 5. Spray samples at regular intervals to determine effects.

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