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#14 Determination of Plasticizer in PVC by IR or FTIR and a Precipitation Method

Submitted by: Arturo Contreras, Visiting Scholar, Center for Chemical Education, Miami University, Middletown, OH; 1996–1997.

I. INTRODUCTION

Description

Students in this experiment will isolate and determine the amount of plasticizer in polyvinyl chloride (PVC). Students will use Infrared Spectroscopy (IR) or Fourier Transform Infrared Spectroscopy (FTIR) and gravimetric techniques in this experiment. Plasticizers are organic compounds added to polymers, like PVC, to facilitate processing and to increase flexibility and toughness of the final product by internal modification of the polymer morphology. Important plasticizers include esters of phthalic acid, and epoxidized soybean oil esters. The most common used plasticizer in PVC is the diester, dioctyl phthalate (DOP).

Student Audience

This experiment is recommended for chemical technology students who have had organic chemistry. Students who have not taken organic chemistry will be able to perform the lab but will not have as clear an understanding of the chemistry.

Goals for the Experiment

By doing this lab the student will:

- demonstrate the use of the IR or FTIR instrument,
- isolate and prepare samples for IR or FTIR,
- read and interpret infrared spectra,
- gravimetrically isolate and quantify plasticizer,
- combine class data for %-plasticizer and determine average and standard deviation,
- identify the plasticizer in PVC, and
- describe what important effects plasticizers have on PVC.

Recommended Placement in the Curriculum

This experiment is recommended for use during a discussion of

- polyvinyl chloride,
- polymer and plastics additives (including plasticizers),
- IR or FTIR, or
- gravimetric analysis.

II. STUDENT HANDOUT

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by IR or FTIR and a Precipitation Method

Scenario

Many commercial polymer resins contain additives which enhance their end-use properties, impact stability, and increase their service lifetime. One such additive is termed a plasticizer because it lowers the glass transition temperature of somewhat rigid amorphous or semi-crystalline polymers to the point where they can be used at or below room temperature. Resin manufactures usually run quality control (QC) testing to make sure the additive concentrations in the production lots are within the specification range. Samples from all production lots are saved for twenty years.

You are a chemical technician in the QC lab of a PVC plant. You have just received many customer complaint samples from a vinyl siding producer who was sued by a national building supply company which was in turn sued by several construction companies because the vinyl siding they used on many homes cracked during the winter months. The company lawyers and executives are frantic at the potential liability and consequently your boss is breathing down your neck and wants a report on these samples by the end of the day.

Safety, Handling, and Disposal

- Wear your safety goggles and lab coat while working in lab.
- Rubber gloves should be worn while performing this lab. Should skin contact occur, wash contaminated area immediately.
- Work in a well ventilated hood.
- Tetrahydrofuran (THF) is flammable and is a dangerous fire risk. Keep all open flames away from this substance. THF is toxic by ingestion and inhalation.
- Dioctyl phthalate (DOP) may reasonably be anticipated to be a carcinogen. Potential symptoms of overexposure are irritation of eyes and mucous membranes.
- Methanol is a dangerous fire risk and needs to be kept away from open flames. It is also toxic by ingestion.
- Read the Materials Safety Data Sheets for all chemicals used in this activity.
- Do not pour any unused mixture down the sink. Any remaining solvent/material must be disposed of in the organic waste container.

Materials

- Tygon® tubing or another plasticized PVC product
- analytical balance
- 2 250-mL Erlenmeyer flasks
- tetrahydrofuran, THF
- 50-mL graduated cylinder
- hot plate
- watch glass
- dropper pipette

- glass slide
- heat lamp
- IR cell holder
- IR or FTIR instrument
- methanol
- 100-mL graduated cylinder
- Büchner funnel
- filtration flask
- evaporating dish
- oven
- (optional) IR pellet press
- PVC reference spectrum
- (optional) dioctyl phthalate (DOP) reference spectrum

Procedure

1. Determination of the IR Spectra of PVC with Plasticizer

a. Weigh 1.0 g of plasticized PVC into a 250-mL Erlenmeyer flask and add 40 mL of tetrahydrofuran.

b. Place the flask with contents on hot plate to heat nearly to boil. Cover the flask with a watch glass while heating.

c. When the PVC is dissolved, use a pipette to add one drop at a time to a glass slide until it is completely covered with the solution. Do not make this film too thick or too thin.

d. Place the slide under a heat lamp to speed up the evaporation of the solvent.

e. Make several slides to insure making a film.

f. After about 30-40 minutes a polymer film is formed on the slide. Strip the film off the slide and mount it on an IR cell holder.

g. Place this sample in the IR or FTIR instrument and scan a spectrum.

h. Identify the IR absorption spectrum of your PVC by comparison with the reference spectrum.

i. Look up the structure of the plasticizer, dioctyl phthalate (DOP). Can you locate the ester band from this plasticizer (which may or may not be present)?

j. (optional) Compare the ester band and any additional (after the PVC bands are eliminated) bands with a DOP reference if available.

2. Removal of Plasticizer from PVC

a. Weigh accurately 1 g of plasticized PVC sample and dissolve it in THF as in Part 1, steps a and b.

b. After sample is completely dissolved, add slowly 100 mL of methanol to precipitate the PVC.

c. Separate the PVC precipitate by filtration through a Büchner funnel and save both the PVC and the filtrate.

d. Dry the PVC precipitate in the oven at 80 °C.

e. Weigh a clean, dry evaporating dish. Place the filtrate in the evaporating dish and evaporate on a hot plate at low heat inside a well ventilated hood.

Caution: Both methanol and tetrahydrofuran will evaporate. This must be done in a fume hood. THF is toxic by inhalation. Review safety precautions.

f. When evaporation is complete, there will be a film on the bottom of the evaporating dish. This is the plasticizer from the PVC sample. Weigh the dish plus film. Calculate the weight of the film and its percent of the initial sample weight. This is the weight-% plasticizer.

g. (optional) Use the film to run an IR spectrum of the plasticizer. This can be compared with the information gained in Part 1, steps i and j.

h. To insure complete removal of plasticizer from PVC, make a KBr pellet of the dry precipitate and run an IR spectra to see if the ester band has been removed.

i. Collect class data on the weight-% plasticizer and determine the mean and standard deviation. Use Q-test (or other statistical means) to check any outlying data.

Questions

1. What are the characteristic absorption bands for PVC? What absorption band identifies the phthalate ester?
2. Discuss the precision of the class data. Is your %-plasticizer within one standard deviation of the mean, two standard deviations of the mean, or etc.? What does this say about the precision and probable accuracy of your data?
3. What are the potential errors in part 2 of this lab and how would they alter the %-plasticizer results.
4. What are plasticizers and why are they used in PVC?
5. Which plasticizer is widely used in polymers?

Questions 6-8 refer to the scenario. Reread it and then answer the questions.

6. What additional tests might you perform to resolve the vinyl siding problem?
7. If you had to go to court, what evidence and documentation would you need?
8. What are some of the questions the plaintiff's lawyer might ask?

References

Department of Polymer Science at the University of Southern Mississippi Web Site, the Macrogalleria; http://www.psrc.usm.edu/macrog/pvc.htm

Ramsay Plastics, The PVC Center Web Site; http://www.ramsay.co.uk

III. INSTRUCTOR NOTES

Determination of Plasticizer in PVC by IR or FTIR and a Precipitation Method

Purpose

To isolate, identify, and quantify the plasticizer in polyvinyl chloride (PVC).

Time Required

This laboratory investigation should take 4–6 hours.

Group Size

It is recommended that students work in pairs on this lab.

Materials

Per class

- Tygon® tubing or another plasticized PVC product
- analytical balances
- tetrahydrofuran, THF
- methanol
- heat lamps
- oven
- IR cell holders
- IR or FTIR instrument
- (optional) IR pellet press
- PVC reference spectrum
- (optional) dioctyl phthalate (DOP) reference spectrum

Per pair of students

- 2 250-mL Erlenmeyer flasks
- 50-mL graduated cylinder
- hot plate
- watch glass
- dropper pipette
- glass slide
- 100-mL graduated cylinder
- Büchner funnel
- filtration flask
- evaporating dish

Safety, Handling, and Disposal

- Students must wear safety goggles and lab coat while working in lab.
- Rubber gloves should be worn while performing this lab. Should skin contact occur, wash contaminated area immediately.
- Students must work in a well ventilated hood.
- Tetrahydrofuran (THF) is flammable and is a dangerous fire risk. Keep all open flames away from this substance. THF is toxic by ingestion and inhalation.
- Dioctyl phthalate (DOP) may reasonably be anticipated to be a carcinogen. Potential symptoms of overexposure are irritation of eyes and mucous membranes.

- Methanol is a dangerous fire risk and needs to be kept away from open flames. It is also toxic by ingestion.
- Read the Materials Safety Data Sheets for all chemicals used in this activity.
- Do not allow students to pour any unused mixture down the sink.
- Provide an organic waste container for any remaining solvent/material. Dispose of this materials according to local, state, or federal regulations.

Points to Cover in Pre-Lab

- Make sure students understand the safety, handling, and disposal procedures of this experiment.
- Discuss the effects of plasticizers in relation to glass transition temperature.
- Define and discuss polymer morphology.
- Demonstrate sample preparation of film and pellet forming for IR.
- Discuss and demonstrate the use of IR and FTIR.
- Discuss and demonstrate interpreting IR spectra.

Plausible Answers to Questions

1. What are the characteristic absorption bands for PVC? What absorption band identifies the phthalate ester?

A: The characteristic IR spectra absorption bands for PVC are: 2950 cm^{-1}, 1450 cm^{-1}, 1285 cm^{-1}, and 1095 cm^{-1}. The absorbance band for the phthalate ester is 1740 cm^{-1}.

2. Discuss the precision of the class data. Is your %-plasticizer within one standard deviation of the mean, two standard deviations of the mean, or etc.? What does this say about the precision and probable accuracy of your data?

A: Answers will vary depending on the data.

3. What are the potential errors in part 2 of this lab and how would they alter the %-plasticizer results.

A: The potential errors discussed should not include errors due to carelessness. Some possibilities include:

a. The PVC does not dissolve completely and traps some plasticizer. This would lower the calculated value of %-plasticizer.

b. Some of the PVC is not precipitated by the methanol. This would increase the calculated value of %-plasticizer.

c. Some of the plasticizer is trapped by the precipitating PVC. This would lower the calculated value of %-plasticizer.

4. What are plasticizers and why are they used in PVC?

A: Plasticizers are organic compounds added to polymers to facilitate processing and to increase the flexibility and toughness of the final product by affecting the internal morphology. It is believed that PVC has many intermolecular attractions which are weakened by the presence of plasticizers. It is assumed that the addition of plasticizer increases the free volume of the polymer and thus affects the glass transition temperature (Tg).

5. Which plasticizer is widely use in polymers?

A: The plasticizer that is widely used is dioctyl phthalate (DOP). DOP is the sole general-purpose plasticizer produced.

6. What additional tests might you perform to resolve the vinyl siding problem?

A: There are many possibilities here. You could run IR or NMR spectra of the recovered plasticizer to show its purity. You could characterize the PVC itself (for example, determine molecular weight). Physical tests could be performed to see if properties change over time. HPLC could be used to determine the type and amount of additives. Electron microscopy of the siding might be used to detect processing problems. Similar tests must be run on the quality control retain sample(s) of the lot(s) sold to the vinyl siding producer.

7. If you had to go to court, what evidence and documentation would you need?

A: Documentation of the methods used including precision and accuracy data would be needed. All the data, spectra, chromatographs of the complaint samples and of the retain samples must be made available along with reference spectra. Shipping records and training records of the analysts should be included. Statistical process control charts showing the manufacturing process was in control and the product lots in question were within specification would also be necessary.

8. What are some of the questions the plaintiff's lawyer might ask?

A: "How can you prove that the complaint samples and the quality control retain samples are from the same lots?" They will ask probing questions about the witnesses and analysts training and credentials. They will certainly question the statistical reliability of the methods and sample analyses.

Extension and Variation

1. Have half of the class determine the %-plasticizer in Tygon tubing and the other half of the class determine the %-plasticizer in PVC pipe. Then compare the results to the properties of the two types of PVC.
2. Have students develop and describe an IR method to quantify the amount of plasticizer in PVC. (Hint: Use a calibration curve.)

References

Department of Polymer Science at the University of Southern Mississippi Web Site, the Macrogalleria; http://www.psrc.usm.edu/macrog/pvc.htm

Ramsay Plastics, The PVC Center Web Site; http://www.ramsay.co.uk