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Laboratory Experiments in Thermal Analysis of Polymers for a Senior/Graduate Level Materials Science Course

Abstract

In the lab accompanying a senior/graduate level Physical and Mechanical Properties of Polymers course, five new lab experiments in thermal analysis of polymers were developed to supplement the classroom lectures and the existing lab exercises. One of these experiments used a new, state-of-the-art rapid heating and cooling differential scanning calorimeter (DSC) to investigate the effects of heating rate and isothermal annealing conditions on the thermal behavior of poly(ethylene terephthalate) (PET). This unique lab experiment was very successful with the students and, because of the high heating and cooling rates, the students were able to perform many experiments within the two hour lab. In this paper we discuss the implementation of these new thermal analysis labs in the course, with an emphasis in comparing the traditional DSC lab with the rapid heating/cooling DSC lab. Feedback from student surveys is also discussed.

Introduction

Physical and Mechanical Properties of Polymers is a co-listed senior level undergraduate course and an elective graduate level course in Materials Science and Engineering at Iowa State University. It consists of two one hour lecture sessions and one two hour lab each week. In the spring of 2009, five new thermal analysis lab exercises were added to the existing labs. These five labs were all in the broader field of thermal analysis. This resulted in a course with 13 labs which were performed by the students over one semester. The topic for these lab experiments are listed below, with the new labs in bold italics.

Lab 1: Synthesis of polystyrene and Nylon 6,6
Lab 2: Gel Permeation Chromatography
Lab 3: Fourier Transform Infrared Spectroscopy
Lab 4: Differential Scanning Calorimetry (DSC)
Lab 5: Rapid Heating/Cooling DSC (RHC DSC)
Lab 6: Wide Angle X-Ray Diffraction
Lab 7: Polarized Optical Microscopy
Lab 8: Tensile Testing
Lab 9: Dynamic Mechanical Analysis (DMA)
Lab 10: Thermogravimetric Analysis (TGA)
Lab 11: Reology
Lab 12: Extrusion
Lab 13: Injection Molding

There were a total of 24 students in the course, so the lab was broken up into 6 different sections (with four students in each section) which met to complete their lab experiments each week.

In this paper, we will begin by discussing how the lab section of this course was implemented. We then describe the five new thermal analysis labs that were developed. Two of these labs (Lab 4 and Lab 5) investigated the thermal transitions in a semi-crystalline polymer, poly (ethylene terephthalate) (PET) using differential scanning calorimetry. However, in Lab 5, the experiments were done using a unique high scanning rate differential scanning calorimeter. Such high scanning rate DSC measurements are just recently becoming available\(^1,2\), and offer unique
advantages for educational lab settings because they facilitate the collection of significant amounts of experimental data in a typical two to three hour lab, and they allow for the collection of data under conditions that more closely resemble the rates found during polymer processing.

### Lab Implementation

Each lab took approximately two hours for the students to complete. For many of the labs, there was only one instrument available, so the six lab sections had to meet at different times during the week. A graduate teaching assistant along with graduate and postdoctoral research associates from the instructor’s research group assisted with running the multiple sections of the same lab throughout the week. There were 12 lab reports written by each four member lab section (Lab 12 and Lab 13 required a joint report). Four of the reports required a “Formal Lab Report” format, four required a “Memo Lab Report” format, two were in the form of a PowerPoint presentation, and two were to be webpage reports.

The write-up assignment for each lab is listed in Table 1 below. For each lab, one group was assigned a presentation format, one group was assigned a web format, and two groups were assigned the Formal and Memo formats.

#### Table 1. Write-up Assignment Matrix

<table>
<thead>
<tr>
<th>Lab #</th>
<th>Group 1</th>
<th>Group 2</th>
<th>Group 3</th>
<th>Group 4</th>
<th>Group 5</th>
<th>Group 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Formal</td>
<td>Memo</td>
<td>Presentation</td>
<td>Formal</td>
<td>Memo</td>
<td>Web</td>
</tr>
<tr>
<td>2</td>
<td>Web</td>
<td>Formal</td>
<td>Memo</td>
<td>Presentation</td>
<td>Formal</td>
<td>Memo</td>
</tr>
<tr>
<td>3</td>
<td>Memo</td>
<td>Web</td>
<td>Formal</td>
<td>Memo</td>
<td>Presentation</td>
<td>Formal</td>
</tr>
<tr>
<td>4</td>
<td>Formal</td>
<td>Memo</td>
<td>Web</td>
<td>Formal</td>
<td>Memo</td>
<td>Presentation</td>
</tr>
<tr>
<td>5</td>
<td>Presentation</td>
<td>Formal</td>
<td>Memo</td>
<td>Web</td>
<td>Formal</td>
<td>Memo</td>
</tr>
<tr>
<td>6</td>
<td>Memo</td>
<td>Presentation</td>
<td>Formal</td>
<td>Memo</td>
<td>Web</td>
<td>Formal</td>
</tr>
<tr>
<td>7</td>
<td>Formal</td>
<td>Memo</td>
<td>Presentation</td>
<td>Formal</td>
<td>Memo</td>
<td>Web</td>
</tr>
<tr>
<td>8</td>
<td>Web</td>
<td>Formal</td>
<td>Memo</td>
<td>Presentation</td>
<td>Formal</td>
<td>Memo</td>
</tr>
<tr>
<td>9</td>
<td>Memo</td>
<td>Web</td>
<td>Formal</td>
<td>Memo</td>
<td>Presentation</td>
<td>Formal</td>
</tr>
<tr>
<td>10</td>
<td>Formal</td>
<td>Memo</td>
<td>Web</td>
<td>Formal</td>
<td>Memo</td>
<td>Presentation</td>
</tr>
<tr>
<td>11</td>
<td>Presentation</td>
<td>Formal</td>
<td>Memo</td>
<td>Web</td>
<td>Formal</td>
<td>Memo</td>
</tr>
<tr>
<td>12/13</td>
<td>Memo</td>
<td>Presentation</td>
<td>Formal</td>
<td>Memo</td>
<td>Web</td>
<td>Formal</td>
</tr>
</tbody>
</table>

In the lecture the week following each lab, the group assigned to give a presentation would present their results in a formal ~20 minute PowerPoint presentation to the class. In addition, the website would be posted by the respective group for the rest of the class to read and to critique.

A student’s grade for a given lab report included both a collective group score assigned by the instructor, and a participation score assigned by the student’s peers. Each person rated the effort of their group mates on each lab report for all members of the group. Ideally, for a group of four students, each student would have a 25% effort. The score given to a particular student was calculated as follows

\[
\text{Student grade} = 75\% \text{ of the report score} + (25\% \text{ of the report score} \times n),
\]
where $n$ is the average reported effort divided by the expected effort.

For example, if a report score is 80% and the average effort rating for a student on a team of 4 is 20%, then the students score is $0.75 \times 80 + 0.25 \times 80 \times 20 / 25 = 76\%$.

However, if the student’s effort in the same example were 30%, the students score is $0.75 \times 80 + 0.25 \times 80 \times 30 / 25 = 84\%$

Overall, this grading policy seemed to work well and encouraged all of the students to contribute to their group lab report.

**Description of the New Thermal Analysis Labs**

*Lab 4: DSC.* In the first new lab, Lab 4: DSC, the students used a traditional DSC to quantify the degree of crystallinity and the temperature of thermal transitions in a poly(ethylene terephthalate), PET, sample removed from a beverage bottle. Two round pieces were punched from the bottle using a leather punch and their masses were measured. These samples were placed into the aluminum DSC pans. Two of these pans were placed on a hotplate set to a temperature well above the melting temperature of the PET, and the polymer was observed to melt. One of these pans was transferred with tweezers into a dewar of liquid nitrogen, the other sample was allowed to cool slowly on the hot plate which was turned off at the same time. Each of these samples (the quickly quenched sample and the slowly cooled sample) were then placed into the DSC and the heat flow rate was recorded at a heating rate of 20 K/min from room temperature to 275 °C. The experimental results were examined to determine such parameters as the glass transition temperature ($T_g$), melting temperature ($T_m$), cold crystallization temperature, and enthalpy of melting for both samples. The students were encouraged to address the following discussion items in their lab reports.

1. Do both specimens exhibit a cold crystallization peak? Explain the reasons for differences, if any.
2. Calculate the degree of crystallinity for the samples tested using the appropriate equations. Are the degrees of crystallinity for the two specimens different? If so explain the origins of the difference?
3. Compare the glass transition temperatures of the two specimens. Is there a relationship between the glass transition temperature and degree of crystallinity?
4. Determine the melting point of each specimen? Does melting point depend on degree of crystallinity?
5. Does the observed enthalpy of melting depend on the degree of crystallinity of the specimen?

*Lab 5: RHC DSC.* In the next lab, Lab 5: RHC DSC, a prototype rapid heating and cooling rate DSC was used to investigate the same PET material. The course instructor’s research team at Iowa State University has been serving as a “Beta”-testing site to evaluate TA Instrument’s (New Castle, DE) pre-commercial rapid-scanning DSC (Project RHC DSC). This advanced instrument is capable of making controlled scanning measurements at heating rates of over 1000 K/min and similarly fast cooling rates. Since these measurements can be performed so quickly (due to the rapid heating and cooling rates of the RHC DSC), it was possible for the students to perform
numerous dynamic and isothermal experiments on the PET samples. In addition, dynamic experiments could be conducted at rates fast enough to completely suppress the cold crystallization effects that were observed in the conventional DSC lab.

The sample pans used in the RHC DSC experiment are nearly ten times smaller than the DSC pans used in Lab 4 (the reduced size is necessary to minimize the effect of thermal gradients at the higher heating/cooling rates). As a result, one of the most challenging tasks for the students was loading the polymer sample into the DSC pans. This was facilitated with the use of a stereo microscope and custom loading tools.

Once the sample was loaded into the instrument, three different defined modules (sets of experiments) were performed. The first module, titled Module 1 (Dynamic measurements), was designed to illustrate the effect of heating rates on the nature of thermal transitions for PET. It involved the following steps.

1. Heat the PET specimen in the RHC DSC above its melting temperature at around 280 °C.
2. Cool the sample to -150 °C at 500 K/min and heat back 500 K/min to 280 °C.
3. After the RHC DSC has cooled down (less than 1 minute), reheat the PET specimen in the RHC DSC above its melting temperature at around 280 °C.
4. Cool the sample to -150 °C at 500 K/min and heat back 20 K/min to 280 °C.

The second module, titled Module 2 (Effect of isothermal crystallization time), was designed to illustrate the effect of isothermal annealing at 125 °C for various times (7, 10, and 15 minutes) on the crystallinity and melting behavior of PET. It involved the following steps.

1. Heat the PET specimen in the RHC DSC above its melting temperature at around 280 °C.
2. Cool the sample to -150 °C at 500 K/min.
3. Heat the PET specimen in the RHC DSC to the isothermal annealing temperature (125°C) and hold for specified annealing time.
4. After completion of the annealing step, cool the DSC at 500 K/min to -150 °C.
5. Perform a heating scan at 500 K/min to examine the effect of the isothermal annealing time.

The third module, titled Module 3 (Effect of isothermal crystallization temperature), was designed to illustrate the effect of various isothermal annealing temperatures (120 °C, 125 °C, 130 °C) on the crystallinity and melting behavior of PET. The following steps were performed in this module.

1. Heat the PET specimen in the RHC DSC above its melting temperature at around 280 °C.
2. Cool the sample to -150 °C at 500 K/min.
3. Heat the PET specimen in the RHC DSC to the specified isothermal annealing temperature and hold isothermally for 10 minutes.
4. After completion of the annealing step, cool the DSC at 500 K/min to -150 °C.
5. Perform a heating scan at 500 K/min to examine the effect of the isothermal annealing temperature.

In the subsequent lab report, the students were asked to address the following discussion items:
Module 1
1) Explain the underlying reasons why a melting transition or cold crystallization transition is not observed on heating at 500 K/min after cooling at 500 K/min? Would you expect melting transition upon heating at 500 K/min if the cooling rate of the prior run had been 20 K/min rather than 500 K/min?
2) Determine the degree of crystallinity, \( T_g \), and \( T_m \) for the heating run performed at 20 K/min after cooling at 500 K/min. Explain the reasons for differences between the heating scans at 20 K/min and 500 K/min.

Module 2
1) What is the origin for the second smaller melting peak in the heating scan at 500 K/min?
2) Compare and describe the variation of both melting points as a function of annealing time.
3) How does degree of crystallinity vary as a function of annealing time? Provide the underlying reasons for the observed trends.
4) Explain the importance of cooling at a fast rate of 500 K/min prior to the isothermal annealing measurements.
5) Does the value of \( T_g \) vary with isothermal annealing time?

Module 3
1) Compare and describe the variation of two melting points as a function of annealing temperature.
2) How does degree of crystallinity vary as a function of annealing temperature? Provide the underlying reasons for the observed trends.
3) If the isothermal annealing temperature was shifted to near the melting point of the polymer, how would that influence the degree of crystallinity? Explain your answer.
4) Does the value of \( T_g \) vary with isothermal annealing temperature?

Lab 9: Dynamic Mechanical Analysis (DMA). In addition to the two calorimetry labs, we also developed a new lab to investigate how the storage modulus of polydicyclopentadiene (polyDCPD) varies with frequency and temperature. The students were then asked to use the principle of time-temperature equivalence to generate a master curve of storage modulus vs. frequency at a particular temperature.

Lab 10: Thermogravimetric Analysis (TGA). The next new lab was developed to use thermogravimetric analysis to determine the carbon black content of a carbon black-filled epoxy sample. This involved measuring the mass loss versus temperature (at a controlled heating rate) for both a neat epoxy and the epoxy/carbon black composite and switching from a nitrogen environment to an oxygen environment to observe how thermal degradation changes in an inert and oxidative environment.

Lab 11: Rheology. The last new lab developed used the tools of controlled stress rheology in a cone and plate geometry to investigate the effect of temperature and strain rate on the viscosity of two polymer/oligomer samples: (1) a silicone viscosity standard and (2) motor oil.
Survey Results

A short survey was given to the students in order to get their perspective on the RHC DSC lab. The survey, shown in the Appendix, asked 12 questions. Questions 1-8 used a five point Likert scale to indicate if they strongly agree, agree, have no opinion, disagree, or strongly disagree with each statement. A number from 1 (for strongly agree) to 5 (for strongly disagree) was assigned to each selection. The next three questions were open ended short answer questions asking the students to list the most interesting aspects of the RHC lab, how the lab could be improved, and how the unique rapid heating and cooling capability of the instrument improved the lab. The final question asked the students to rate the labs from best (1) to worst (12). A total of 23 students responded to the survey.

The first eight questions/comments from the survey are listed in Table 2 below along with the average response for each question.

<table>
<thead>
<tr>
<th>Question/Comment</th>
<th>Average Response</th>
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</thead>
<tbody>
<tr>
<td>1. This RHC DSC lab was a valuable educational experience.</td>
<td>1.5</td>
</tr>
<tr>
<td>2. The RHC DSC was easier to use than a conventional DSC.</td>
<td>3.2</td>
</tr>
<tr>
<td>3. The RHC DSC lab was better than the conventional DSC lab because we could perform more experiments in the allotted lab time and didn’t have to wait as long for the tests to finish.</td>
<td>1.7</td>
</tr>
<tr>
<td>4. The lab experience sufficiently covered the concepts influencing polymer crystallinity.</td>
<td>1.7</td>
</tr>
<tr>
<td>5. My understanding level of polymer crystallinity improved after the RHC DSC lab.</td>
<td>2.0</td>
</tr>
<tr>
<td>6. I would recommend that the RHC lab be a part of the curriculum in the future.</td>
<td>1.4</td>
</tr>
<tr>
<td>7. The RHC lab successfully facilitated my understanding about the rigid amorphous phase in PET.</td>
<td>1.8</td>
</tr>
<tr>
<td>8. I found the RHC DSC lab to be interesting.</td>
<td>1.6</td>
</tr>
</tbody>
</table>

There was an overwhelmingly positive response to the RHC DSC lab. All of the students either agreed or strongly agreed that the RHC DSC lab was a valuable educational experience (question 1). Nearly all the students either agreed or strongly agreed that the RHC DSC lab was better than the conventional DSC lab because it allowed the students to perform more experiments in the allotted lab time (question 2). In general the students felt that it improved their understanding of polymer crystallinity (question 5) and that it should become a regular part of the curriculum for that course (question 6). In question 3, many students disagreed that the RHC DSC was easier to use than the conventional DSC. This is most likely due to the difficulty that the students had in loading the small samples into the very small sample pans in the RHC DSC experiment.

In the short answer response to the question “What was the most interesting aspect of the RHC lab?”, several students mentioned that being able to use a research grade, unique instrument such as the RHC DSC was very interesting. Others commented that they found it interesting to
compare the results obtained from the conventional DSC (at much slower heating and cooling rates) with the results from the RHC DSC. Some comments for this question are shown below.

- *I think it was really neat that we got to use a very rare machine as undergrads.*
- *I was impressed that it was possible to heat and cool rapid enough to prevent crystallization. This supported the fact that crystallization is a kinetic behavior.*
- *It was good to see how heating and cooling rates affected the crystallinity of the polymer. It helped me understand the time dependence of phase transformations.*
- *The ability to contrast it with the standard DSC which was done earlier.*
- *It was interesting to be able to look at the rigid amorphous phase in PET. Also, it was exciting to use such a rare machine.*

Short answer response to the question “How could the RHC lab be improved” included making it easier to load the samples into the DSC, and investigating different polymer systems.

Overall, the RHC DSC lab tied (with the polarized optical microscopy lab, not discussed here) for the best lab when the students ranked the labs from best to worst. In all cases, the students rated the RHC DSC lab as better than the conventional DSC lab. The ranking of the labs as determined by the student surveys are listed below from best to worst:

<table>
<thead>
<tr>
<th>Lab</th>
<th>Average Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab 5: Rapid Heating/Cooling DSC (RHC DSC)</td>
<td>4.6</td>
</tr>
<tr>
<td>Lab 7: Polarized Optical Microscopy</td>
<td>4.6</td>
</tr>
<tr>
<td>Lab 8: Tensile Testing</td>
<td>4.7</td>
</tr>
<tr>
<td>Lab 1: Synthesis of polystyrene and Nylon 6,6</td>
<td>5.4</td>
</tr>
<tr>
<td>Lab 11: Reology</td>
<td>6.6</td>
</tr>
<tr>
<td>Lab 4: Differential Scanning Calorimetry (DSC)</td>
<td>6.9</td>
</tr>
<tr>
<td>Lab 9: Dynamic Mechanical Analysis (DMA)</td>
<td>6.9</td>
</tr>
<tr>
<td>Lab 12 and 13: Extrusion &amp; Injection Molding</td>
<td>7.3</td>
</tr>
<tr>
<td>Lab 2: Gel Permeation Chromatography</td>
<td>7.6</td>
</tr>
<tr>
<td>Lab 3: Fourier Transform Infrared Spectroscopy</td>
<td>7.6</td>
</tr>
<tr>
<td>Lab 6: Wide Angle X-Ray Diffraction</td>
<td>8.0</td>
</tr>
<tr>
<td>Lab 10: Thermogravimetric Analysis (TGA)</td>
<td>8.5</td>
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</tbody>
</table>

**Conclusion**

The five new lab sessions which were added to this course provided the students with new experiments in the often under-represented area of thermal analysis of polymers. These labs offered the students distinct didactic outcomes, while still retaining an element of research uncertainty and inquiry based learning. The RHC DSC lab used a highly specialized instrument to enable the students to perform a number of experiments in one two-hour lab session, and it is clear from survey results that students benefited from access to this unique instrument.
widespread availability of such an instrument is currently limited, many of these experiments can be performed using a conventional DSC instrument, albeit over a considerably longer period of time. In addition, it is expected that higher heating and cooling rates will continue to be incorporated into new generations of DSC instruments.

Acknowledgement

We thank TA Instruments for providing the RHC DSC used in this laboratory course.
# RHC DSC Lab – Class Survey

I am interested in your thoughts about our RHC DSC lab. Specifically, I am hoping to write a paper for an engineering education journal describing the project. There are no right or wrong answers. Just tell me what you think. Read each item carefully and circle the response (Strongly Agree, Agree, No Opinion, Disagree, Strongly Disagree) which best describes your feelings about each item.

1. This RHC DSC lab was a valuable educational experience.
   - Strongly Agree
   - Agree
   - No Opinion
   - Disagree
   - Strongly Disagree

2. The RHC DSC was easier to use than a conventional DSC (such as a Q20 DSC).
   - Strongly Agree
   - Agree
   - No Opinion
   - Disagree
   - Strongly Disagree

3. The RHC DSC lab was better than the conventional DSC lab because we could perform more experiments in the allotted lab time and didn’t have to wait as long for the tests to finish.
   - Strongly Agree
   - Agree
   - No Opinion
   - Disagree
   - Strongly Disagree

4. The lab experience sufficiently covered the concepts influencing polymer crystallinity.
   - Strongly Agree
   - Agree
   - No Opinion
   - Disagree
   - Strongly Disagree

5. My understanding level of polymer crystallinity improved after the RHC DSC lab.
   - Strongly Agree
   - Agree
   - No Opinion
   - Disagree
   - Strongly Disagree

6. I would recommend that the RHC lab be a part of the MATE 453/ MSE 553 curriculum in the future.
   - Strongly Agree
   - Agree
   - No Opinion
   - Disagree
   - Strongly Disagree

7. The RHC lab successfully facilitated my understanding about the rigid amorphous phase in PET.
   - Strongly Agree
   - Agree
   - No Opinion
   - Disagree
   - Strongly Disagree

8. I found the RHC DSC lab to be interesting.
   - Strongly Agree
   - Agree
   - No Opinion
   - Disagree
   - Strongly Disagree
Short Answer:
Describe briefly the most interesting aspect of the RHC lab.

What changes would you make to improve the RHC lab?

How did the unique rapid heating and cooling capability of the instrument improve the lab?

Please rate all of the labs from Best (1) to worst (12)

Lab 1: Synthesis of PS and Nylon 6,6
Lab 2: Gel Permeation Chromatography
Lab 3: Fourier Transform Infrared Spectroscopy
Lab 4: DSC
Lab 5: RHC DSC
Lab 6: Wide Angle X-Ray Diffraction
Lab 7: Polarized Optical Microscopy
Lab 8: Tensile Testing
Lab 9: DMA
Lab 10: TGA
Lab 11: Reology
Lab 12/13: Extrusion & Injection Molding
Bibliography
