Practical 2P11

Mechanical properties of polymers

What you should learn from this practical

Science

This practical will help you to understand two of the most important concepts in applied polymer science:

- The Boltzmann Superposition Principle
- Time-Temperature Superposition.

Safety

We are using a class 2 laser for this practical. Although the power of the laser is low, please treat it with caution and good practice for use of lasers. Ensure that there is no opportunity for the beam to be directed into your eye, this means:

1) Keeping your face out of the area of the beam;
2) Avoiding the risk of unexpected reflections. This means particular care should be taken when aligning or adjusting the equipment, and removing jewellery that might reflect;
3) Do not adjust or remove the black enclosures that are in place around the equipment.

In addition you will use hot water – this can usually be straight from the hot tap, but please be aware of any potential scald risk.

Practical Skills

- Good practices for data collection, manipulation, analysis and presentation.

- Experimental choices in planning the methodology such as how precisely it is important to take measurements or control parameters, how many repeat measurements to take etc.
- Recognising sources of error.
- Estimating the magnitude of errors.

Overview

This practical consists of three experiments:

Experiment 1: To verify that polyethylene exhibits linear viscoelastic properties.

Experiment 2: To verify the Boltzmann Superposition Principle.

Experiment 3: To predict long term creep using the Time-Temperature Superposition Principle.

Experimental details

Introduction

You will measure creep in polyethylene at temperatures that are close to ambient.

Apparatus

A torsional creep machine is provided. The specimen is a rectangular strip of length l, breadth b and thickness h. The specimen should be mounted vertically, with its lower end held rigidly, and its upper end subjected to a constant torque (twist) T, the angle of twist $\theta$is given by:

$$\theta = \frac{lTJ}{Q} \qquad (1)$$

where ; J is the compliance of the specimen

Q is a geometrical form factor equal to: $\frac{1}{3}bh^3\left(1 - 0.63\frac{h}{b}\right)$ (2)

In the torsional creep machine, torque is applied by switching on a current I in a coil that lies in a magnetic field. Therefore:

$$T = kI \quad (3)$$

where k is a constant for the coil (k = 0.00171 Nm/A).

If J depends on time t (i.e. the specimen is viscoelastic), θ must also be time-dependent. Equations (1) and (3) can then be combined and written as:

$$J(t) = \frac{Q}{lkI}\theta(t) \quad (4)$$

θ can be expressed in terms of the throw L of the optical lever and the deflection x of the cross hair:

$$\theta = \frac{x}{2L} \quad (5)$$

L is determined by the length between the laser and the mirror (about 1m).

Specimen

The specimen was cut from an extruded high density polyethylene sheet. The dimensions of the specimen are l = 100mm, b = 10mm, h = 1mm.

Experiment 1

(a) Set the current to give an initial deflection in the range 1-2cm; then switch off. Let the specimen recover until movement of the cross-hair is negligible. Zero the cross-hair.

(b) Switch on the current and make measurements of deflection every 10 seconds, for a total of 30 seconds. Switch off the current.

(c) Repeat steps (a) and (b) for initial deflections in the range 3-4cm, 5-6cm, 8-9cm, and 11-12cm.

(d) To check that the polyethylene exhibits linear viscoelastic mechanical behaviour (over the stress range tested here), plot graphs of deflection versus current for t = 10s, t = 20s and t = 30s (all on one set of axes).

Experiment 2

Obtain data for deflection versus time when the specimen is subjected to a **pulsed** load as follows:

(a) Set the current so that the initial deflection lies in the range 8-9cm, *note the current setting*, and then switch off. Let the specimen recover for sufficient time.

(b) Switch on the current and start the watch (t = 0)

(c) Record deflection at t = 10, 20, 30, 40, 50 and 60s. At 60s, switch off the current (but let the watch continue to run) and immediately record deflection again.

(d) Record deflection at 70, 80, 90, 100, 110 and 120s. At 120s, switch on the current (and let the watch continue to run) and immediately record deflection again.

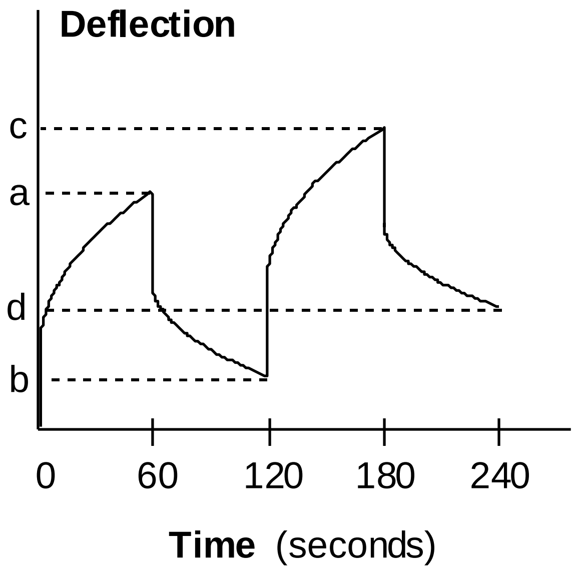
(e) Record deflection at 130, 140, 150, 160, 170 and 180s. At 180s, switch off the current (but let the watch continue to run) and immediately record deflection again.

(f) Record deflection at 190, 200, 210, 220, 230, and 240s. Stop!

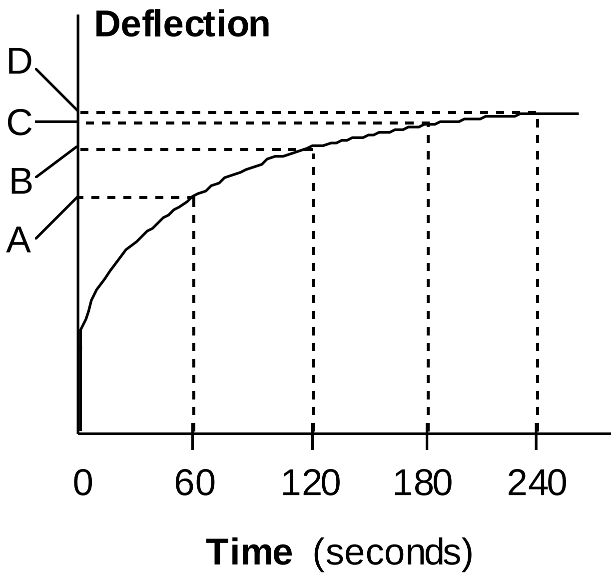
Before continuing with the experiment, allow the unstressed specimen to recover for at least 10 minutes. This time can be spent constructively as follows:

(a) Plot your recorded values of deflection versus time.

(b) Use your plot to predict the outcome of an experiment in which the specimen is subjected to a **constant** load:



Measured results of pulsed load



Predicted results of constant load (using Boltzmann Superposition Principle):

A	=	a
B	=	a + b
C	=	b + c
D	=	c + d

Now perform the following constant load experiment to check your prediction:

(a) With the current set to the same value as in the pulsed load experiment, switch on the current and start the watch (t = 0)

(b) Record deflection at t = 5, 10, 20, 30, 60, 90, 120, 150, 180, 210 and 240s.
(c) Also note the specimen temperature.
(d) Switch off the current.
(e) Plot your recorded values of deflection versus time on the same axes as your predicted results.

The steps (a) - (c) above also provide data that you will need in Experiment 3.

Experiment 3

Raise the specimen temperature to approx. 50°C by immersing the specimen a water bath. The temperature should be monitored throughout the experiment and kept within a reasonable window by adding warm or cool water to the bath as necessary. Repeat the steps (a) - (d) as detailed immediately above.

Data for 30ºC and 40ºC are appended to these instructions. You should use these data, along with those you have taken for room temperature in Experiment 2 to provide the basis for the analysis of the time-temperature superposition described below. As time permits, you may wish to take measurements at a variety of temperatures for yourself for inclusion in your analysis. Please do not exceed 60ºC.

Calculate $J(t)$ for all data points, and plot against (log t). All data should be plotted on a single graph.

The principle of Time-Temperature Superposition states that the creep compliance (for a static load) applied at a reference temperature, T_o, may be obtained at times outside the experimentally accessible range by performing experiments at higher or lower temperatures. The physical basis of the principle can be illustrated by considering a standard linear solid (Zener) model, characterised by a single relaxation time.

For this model, the creep compliances at temperatures T_o and T are:

$$J_{T_o}(t) = J_U + [J_R - J_U]\left[1 - \exp\frac{-t}{\tau_{T_o}}\right] \quad (6a)$$

$$J_T(t) = J_U + [J_R - J_U]\left[1 - \exp\frac{-t}{\tau_T}\right] \quad (6b)$$

where: J_U is the creep compliance of the specimen for very short loading times (unrelaxed), assumed to be independent of temperature,

J_R is the creep compliance of the specimen for very long loading times (relaxed), also assumed to be independent of temperature

τ_{T_o} is the relaxation time at temperature T_o

τ_T is the relaxation time at temperature T.

If the relaxation time depends on temperature according to the Boltzmann function, then

$$\tau_T = a_T \tau_{T_o} \quad (7)$$

where

$$a_T = exp\frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T_o}\right] \quad (8)$$

Equations (6) and (7) can be combined to give:

$$J_T(t) = J_U + [J_R - J_U]\left[1 - \exp\frac{-t}{a_T \tau_{T_o}}\right] = J_{T_o}\left(\frac{t}{a_T}\right) \quad (9)$$

This equation states that it is possible to obtain the creep compliance at T_o at a time $\frac{t}{a_T}$ by measuring the creep compliance at time t at a different temperature T.

The following graphical procedure enables you to compute both $J_{T_o}\left(\frac{t}{a_T}\right)$ and ΔH:

(a) Take T_o as room temperature.

(b) Plot $J(t)$ versus log t for all data using separate x co-ordinate data in each case. (In Excel this can be achieved by entering repeating blocks of data in the first column and inserting the various compliance data sets for different temperatures in the next column. The chart should be plotted as ‘XY (scatter) plot with no lines connecting the data.) Plot the chart with all the data included.

(c) Now add a constant (e.g. start with 1) to the value of log t for the data set at 30ºC. The 30ºC data will have shifted along the x axis. Vary the value of the constant that you add until the data points with high compliance at T_o match up with and overlap the data points at low compliance at the lower temperature. The constant that you added will be –log a_T.

(d) Repeat (c) for the ~40°C and ~50°C data. In this way you will generate a master curve for the compliance at T_o.

(e) Plot log a_T versus $\frac{1}{T}$ and so obtain ΔH.

The Report

Objectives

- Briefly state the objectives of the practical.
- Briefly describe the two principles that are tested in this practical.

Experimental procedure

- Describe any modifications made (or precautions taken) to reduce errors.
- Describe any steps taken to quantify the reproducibility of your results.
- **Do not** copy the information provided in these guidelines; simply refer to it as necessary.

Results

- Present all graphs and determine numerical quantities as requested above.
- Include error bars on all graphs.
- Consider carefully what your graphs represent. What is the correct function or fit to use for the data? Make it clear how you have used the data to do any further calculations and to draw the conclusions you have from the data.

Discussion

- Explain how your results should be interpreted in the context of each experiment's objective.
- Discuss the practical relevance of the two principles that you have tested.
- What are the limitations of these principles?

Conclusions

- List those conclusions that your work substantiates.

Suggested reading

- **Principles of Polymer Engineering**, N.G. McCrum, C.P. Buckley and C.B. Bucknall, Oxford University Press, 1988.
- **Fundamentals of Polymer Science**, P.C. Painter and M.M. Coleman, Technomic, 1994.
- **Introduction to Physical Polymer Science**, L.H. Sperling, John Wiley & Sons, 1992 (2nd edition)
- **Fundamental Principles of Polymeric Materials**, S.L. Rosen, John Wiley & Sons, 1993 (2nd edition)
- **Textbook of Polymer Science**, F.W. Billmeyer, John Wiley & Sons, 1984 (3rd Edition).

Appendix

Data for the compliance of the polyethylene bar measured in torsion at 30ºC and 40ºC. These data are to be used in conjunction with your own data from Experiment 2 and Experiment 3 to create the master curve for time-temperature superposition.

time (s)	$J_{30^oC}(t)$ Pa^{-1}	$J_{40^oC}(t)$ Pa^{-1}
5	3.73E-7	4.12E-7
10	3.91E-7	4.37E-7
20	4.16E-7	4.64E-7
30	4.40E-7	4.93E-7
60	4.61E-7	5.32E-7
90	4.79E-7	5.57E-7

120	4.93E-7	5.81E-7
150	5.04E-7	6.02E-7
180	5.11E-7	6.16E-7
210	5.21E-7	6.26E-7
240	5.28E-7	6.34E-7