Practical 1P5

Polymers - Molecular weight effects

What you should learn from this practical

Science

One of the themes of the Structures of Crystalline and Glassy Materials lecture course is that molecular weight, and the ability to control and characterise it, are very important considerations when one works with polymeric materials. In this practical, you will explore how some mechanical properties are affected by molecular weight. The average molecular weight can be controlled effectively and easily by altering the number of **cross-links** between molecules, either during or after the formation of polymer chains from monomer. For flexible polymers, a higher average molecular weight is associated with a greater degree of chain entanglement; a large density of cross-links imposes a similarly enhanced level of interchain association.

Practical Skills

- Good practices for data collection, manipulation, analysis and presentation
- Recognising and minimising sources of error

Overview

This practical consists of three experiments:

Experiment 1: Cross-link density in gelatine.

Experiment 2: Cross-link density in rubber.

Experiment 3: Cross-link density and the glass transition temperature.

Timetable

Day 1:

- Read this entire set of guidelines
- Familiarisation with equipment
- Prepare jellies as required for Experiment 1
- Perform either Experiment 2 or 3; analyse data as suggested below

Day 2:

- Finish Experiment 1; analyse data as suggested below
- Perform the remaining Experiment from 2 and 3; analyse data as suggested below
- Generate remaining sections of write-up.

Experiment 1: Cross-link density in gelatine

Introduction

Ordinary gelatine is partially hydrolysed collagen - i.e. it is a partially degraded protein. When dissolved in hot water, the gelatine molecules adopt a random coil conformation. On cooling, the conformation changes to approximately helical, and intermolecular hydrogen bonds are able to form. The assembly of molecules into a three-dimensional, elastomeric, hydrogen-bonded network is responsible for the “setting” of jelly. Each cross-link can be regarded as a site from which four chain segments extend in different directions, in which case rubber elasticity theory predicts that:

$$E = 6C_x RT$$

where E = Young’s modulus

C_x = cross-link density (moles per unit volume)

R = molar gas constant = 8.31 $\mathrm{J.mol^{-1}.K^{-1}}$

T = absolute temperature

In other words, Young's modulus is directly proportional to the density of cross-links, and therefore increases with effective molecular weight.

Young's modulus can be determined by placing a spherical object on the surface of the set jelly, and measuring the depth of the indentation:

$$E = \frac{3mg\left[1-\nu^2\right]}{4h^{3/2}r^{1/2}} \quad \text{(Hertz equation)}$$

where m = mass of sphere

r = radius of sphere

g = acceleration due to gravity = 9.8 m s^{-2}

h = depth of indentation

ν = Poisson's ratio of jelly (you should be able to estimate this on the basis of what you learned in your **Elasticity** course!)

Equipment

- Five 100 ml, heat-resistant, graduated beakers
- Levelling device (petri dish containing sand)
- Electric kettle
- Jelly
- Refrigerator
- Steel bearing (approx. 3.5 cm diameter)
- Tissues
- Tongs that can grip the bearing firmly (Sainsbury's kitchen tongs are good)
- Metric ruler or graph paper
- Thermometer

Method

Prepare solutions of jelly at 1×, 2×, 3×, 4× and 5× the manufacturer's recommended concentration. Each concentration should have a total volume of 50ml. The solutions should be at least 5 cm deep in each beaker. Cover the beakers, and let the jelly set in the refrigerator. (At this stage, continue with experiment 2, and return to experiment 1 on the second day of your practical.)

Carefully place the steel bearing in the centre of each sample (the levelling device will be needed here), and measure the depth of indentation. Clean the bearing when it is moved between samples. Use the results, and appropriate values of m, r, g, ν, R and T, to estimate C_x for the five samples.

Analysis

- Plot E and C_x as a function of solution concentration.
- Calculate the ratio (C_x / solution concentration) for each sample.
- Comment on these results.
- Discuss the likely sources of error in your experiments.

Experiment 2: Cross-link density in rubber

Introduction

Two types of cross-link occur in rubber. Mechanical cross-links are entanglements, while chemical cross-links are imposed in the form of covalent sulphur bridges when rubber is vulcanised. It is the chemical cross-links that limit the extent to which rubber can creep under load. Rubber elasticity theory leads to the following equation for the load-extension behaviour of elastomers:

$$\sigma_n = NkT\left[\lambda - \frac{1}{\lambda^2}\right]$$

where σ_n = nominal stress (load / initial cross-sectional area)

λ = extension ratio (final length / initial length)

N = number of **chains** per unit volume

k = Boltzmann's constant = 1.38×10^{-23} J K^{-1}

T = absolute temperature

The effective number of chains per unit volume increases as the number of cross-links increases.

Equipment

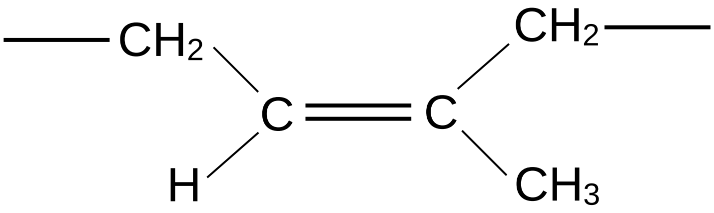
- Straight balloons (as used for balloon sculptures)
- Spring balance
- Metric ruler
- Vernier callipers
- Ballpoint pen
- Thermometer

Method

Fold a balloon over the hook of the spring balance. Mark two parallel lines, several centimetres apart, across the balloon. Use the balance and the ruler to obtain load-extension data for the balloon rubber. You should aim to obtain an extension ratio of approximately 3 at full scale deflection on the balance: fold the balloon as necessary prior to taking your measurements. The ruler and callipers can be used to determine the load-bearing cross-sectional area of the unstressed rubber. Be careful not to compress the rubber while measuring its thickness. Repeat the experiment on each of two additional balloons.

Analysis

- Convert your measurements of load to values of nominal stress.
- Plot your data in a form that allows you to determine the value of N for each balloon most easily.
- Take the density of balloon rubber as being 950 kg m^{-3} and estimate the weight of a typical polymer chain in the rubber of each balloon. Note that “chain” refers to a molecular segment between cross-links.
- The monomer repeat unit of balloon rubber is shown below:



  Estimate the typical number of monomers between cross-links in each balloon.

  1 Da (a.m.u.) = 1.66×10^{-27} kg.

- Discuss the significance of any variation between the answers obtained for the different balloons.

- Discuss the likely sources of error in your experiments.
- How would you expect the behaviour of the balloons at 30°C to compare with their behaviour at 20°C?

Experiment 3: Cross-link density and the glass transition temperature

Introduction

In Experiments 1 and 2, you have learned that the stiffness of elastomers is an increasing function of the cross-link density. However, the equations describing rubber elasticity do not remain valid as cross-link density increases indefinitely. Eventually, the chain segments between cross-links are not flexible enough to permit rubber-like deformation. The polymer instead exhibits many of the load-extension characteristics of an inorganic glass, in which the amorphously ordered chains are highly cross-linked and conformationally rigid. Thus, increasing the cross-link density raises the glass transition temperature of the polymer.

At temperatures above its glass transition, an elastomer can readily deform in response to an applied load, and most of the energy of loads applied over short timescales can be recovered quickly. This is why rubber bands serve as successful catapults in schools, and rubber sheet is used in trampolines. At temperatures below its glass transition, the elastomer will again deform recoverably in a short period of time (if the stress does not exceed the elastic limit), although the modulus linking elastic stress and strain may be orders of magnitude higher than for the rubber. However, at temperatures close to the glass transition, where the molecules are on the verge of acquiring flexibility, much of the energy of an impact is dissipated irrecoverably in the microstructure.

The different “speeds” of squash balls are achieved by using cross-link density to tailor how close the glass transition of the ball lies to room temperature.

Equipment

- Double yellow-, yellow-, red-, and blue-dot squash balls. (The blue-dot balls are the fastest, and will rebound viciously from most surfaces that they strike during a game. In contrast, the double yellow-dot balls usually have the rebound characteristics of a blob of porridge.)
- Liquid nitrogen
- Metre rule
- Tongs
- Thermometer

  Safety note: Liquid nitrogen can cause nasty burns. Wear a lab coat, eye protection and insulating gloves, and use the tongs provided to handle the balls.

Method

Immerse a squash ball briefly in the liquid nitrogen and then remove it. When its surface temperature has warmed to -30°C, drop it from a height of 1 m alongside the metre rule, and measure the height of the rebound.

> **Safety note:** DO NOT drop the ball when its temperature is below -30°C, or from a height greater than 1 m as it may shatter. If the ball does shatter, do not handle the pieces until they have warmed up.

Repeat the measurement at 5°C intervals up to room temperature. Then repeat the entire experiment with each of the other types of ball.

Analysis

- Plot rebound height as a function of temperature for each type of ball.
- Estimate the glass transition temperature for each type of ball.
- Relate your findings to the performance of each type of ball.
- Explain why advanced squash players whack the daylights out of the ball before starting a game.

Lab Book

This practical will be lab book only assessed. It will be marked out of 3, marks are awarded for the quality of your lab notebook entry. In awarding these marks the Senior Demonstrator will consider all of the following:

- **Presentation and completeness of results** (1 mark), where they'll check you have followed the "best practice guidelines in this document (e.g. "Things to check section") and whether you have included and correctly described all the data/results specified in the script.
- **Data analysis and errors** (1 mark), where we will evaluate if the analysis of data, including error analysis, is adequate.
- **Interpretation of results and conclusions** (1 mark), where we will evaluate your understanding of the experiment, its results and how you summarize it all in some brief but meaningful conclusions.

Suggested reading

Introduction to Physical Polymer Science, L H Sperling, John Wiley & Sons, 1992 (2nd Edition).

Fundamentals of Polymer Science, P C Painter and M M Coleman, Technomic, 1994.