KINETICS OF SWELLING APPLIED ON GELATINE

A study using
Fluid Dynamic Gauging
respectively
Gravimetric Measurements

A Master's thesis by

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ABSTRACT

This report is about the measurements of swelling gelatine films of different thickness and at different temperature. The research has been mainly focused on finding a suitable model. Results have shown that the new Pseudo-Sigmoidal Model (PSM) is superior to previous quasi-second order models such as the Robinson and Ofner model. It has also been shown that gelatine's swelling can be divided into three different states: amorphous, intermediate and crystalline, and they can be described via a simple model. Gelatine film does not swell beyond the initial amorphous state when it is above the glass temperature. Calculations have shown that the long dismissed Hofmeister model is identical to the current Ofner model.

Keywords: gelatine, swelling, Hofmeister, Robinson, Ofner, pseudo-second order model, pseudo-sigmoidal model (PSM), gravimetric measurements, fluid dynamic gauging (FDG), bio-polymers, anisotropic material, Arrhenius equation, physical chemistry, photography, pharmaceutics

CONTENTS

Abstract 1

Background and history 5

Aims 6

Theory 7

Gels 7

Physical chemistry in polymers 7

Swelling 8

Models for the kinetics of swelling for gels and polymers 8

Gelatine 9

Swelling properties of gelatine 9

Modelling of the kinetics of swelling for gelatine 10

Introduction to Rheology 11

Dynamic mechanical analysis 12

Fluid dynamic gauging (FDG) 13

Material 15

Methods 16

Preparation of gelatine samples 17

Optimising drying speed of gelatine films 17

Swelling experiments 17

Method A – Gravimetric measurements 18

Method B – Fluid Dynamic Gauging (FDG) 19

Temperature control for method A and B 20

Analysis 21

Density measurements of different gelatine states 21

Accuracy measurements of pipettes 22

Differential Scanning Calorimeter measurements 22

Rheology 22

Evaluation of data 22

Results 23

Swelling 23

Method A – Gravimetric Measurements 23

Method B – Fluid Dynamic Gauging (FDG) 24

Models for kinetics of swelling for gelatine 25

Rheological Studies 27

Enthalpy and glass transition point measurements 29

Density measurements 29

Solid amorphous gelatine film 29

Liquid gelatine solution 29

Optimisation of drying procedure 30

Discussion 31

Experiments 31

Method B 31

Swelling 31

Different states of swelling 31

Temperature and glass transition 32

Transitional regions 32

Intermediate region 33

Region IV, or odd swelling behaviour? 33

Models 34

Comparison between the pseudo-second order models 34

Time-dependent model for polymers in general 35

The Pseudo-Sigmoid Model (PSM) 36

Drying film 37

Storage of film 37

Gelatine gel density 37

Volume fraction of solvent......37
Dry gelatine film density......38
Conclusions......39
Acknowledgements......40
Abbreviations......40
References......41
Private communications......42
Appendix......43
I: Procedure for film making......43
II: Coefficients for models......43
Kinetics model......43
III: Calculations......44
The Robinson model......44
VI: Data series......45
Rheology......45
Density measurements......51
Pipette accuracy......52
Kinetics experiments......54

BACKGROUND AND HISTORY

I was given the opportunity to visit the Wilson's and Chew's research group at the University of Cambridge, to utilise the Fluid Dynamic Gauging (FDG) that measures the thickness of deposits or films in situ. For this M.Sc. thesis I've studied the thickness of gelatine. FDG has several benefits over other methods, such as infrared, microwave and other techniques of measuring thicknesses in situ, mainly it is uncomplicated and fairly straight forward and cost efficient. (WILSON, 2000)

Gelatine is a protein based biopolymer and the interest for gelatine started with the photographic industry, when they moved away from wet glass plates, used for daguerreotype and the collodion process, covered with a light sensitive emulsion often with silver halides, to put the silver halides into gelatine films resulted in dry photographic glass plates. Later the gelatine film with silver halides was put on a cellulose based back to capture the light.

For the past decades has the interest for gelatine mostly been within the pharmaceutical industry where it can be used as a release mechanism of the active substance. Gelatine has parallel to this development also been frequently used within the food industry, where it makes out the base of jellies, candies and act as a general thickener. (ARVANITOYANNIS, 2002) The relevance of gelatine is still very high, especially considering that the world market price is currently reaching record high prices, and increased with 40% over in 2012 due to several factors such as new EU regulations on pig farming, a leather shortage in China and difficulties in the Brazilian pig industry. (SVENSKA DAGBLADET, 2013)

Despite that gelatine has been widely used and studied for well over a century, where the peak was around 1920 with Edith B. Shreve (SHREVE 1918; SHREVE 1919) being the one of the leading authorities on gelatine swelling. Also worth mentioning are S.E. Shepard (SHEPARD 1923), Procter, Wilson and Loeb (LOEB, 1922), which all did a substantial amount of research to investigate gelatine's swelling behaviour. Despite this is gelatine's factual swelling kinetics and mechanisms still largely veiled in mystery. There have been a few attempts to solve the enigma regarding the swelling mechanism, notably C.M. Ofner III (OFNER, 1986; OFNER 1987) who did his Ph.D. thesis on the subject, which in essence only re-produced Franz Hofmeister's (HOFMEISTER, 1890) research on swelling, especially when it comes to modelling, as I will show. Ofner's research was heavily influenced by Ian D. Robinson's (ROBINSON, 1964) kinetics experiments, and borrowed many of his ideas, especially his quasi-second order kinetics, but largely ignored Robinson's affection for the Flory theory of swelling.

AIMS

The aims of these experiments were to study the kinetics of swelling for gelatine, and if possible to find a mathematical model that explains it. But also to evaluate the Fluid Dynamic Gauging (FDG) method (WILSON, 2000) a non-invasive method to measure the distance to a fix surface, and it share many principal similarities with equipment especially designed to study the swelling of gelatine films developed by Kodak (LEWIS, 1950). The FDG method has been developed at the University of Cambridge at the Department of Chemical Engineering and Biotechnology by Wilson & Chew. (WILSON, 2000; CHEW, 2004-I; CHEW, 2004-II; CHEW, 2006; CHEW, 2007)

Questions to be answered:

- What are the properties of the gel during swelling and do they change?
- How does temperature affect the swelling trends?
- With which states can the swelling profile of gelatine be described?
- Can a more precise model be found to describe the swelling of gelatine?

THEORY

Gels

A gel is a solution that has hardened to an elastic semi-solid mass, or rather a coagulated colloid. This is unlike a sol, i.e. a stabilised colloid dispersion. Gels are foremost formed with macromolecules, for instance polymers, which can be of either organic or inorganic origin. A gel has a network, which is formed out of the solution or dispersion with the gelling substance, which then swells somewhat in a solvent. The gel point is when a molecule has a remote connection across the material in question, and in this process may covalent bonds form, which makes this process become irreversible. It is however possible for gels to only be held together with physical forces, which in term allows the gel to return to its colloid solution. (Nationalencyklopedin, 2013-III)

It is important to differentiate between lyogels and xerogels. The lyogel is a gel with liquid content, while a xerogel is one where it has been removed, via for instance by drying, where the three dimensional network has collapsed. The xerogel can be reversed into a lyogel, when it is subjected to a suitable solvent, which will lead the gel to swell considerably and rapidly. Examples of xerogels are dried gelatine and dried agar-agar gels. (Nationalencyklopedin, 2013- III)

Physical chemistry in polymers

Polymer's physical state can undergo several phases, which include amorphous, mesomorphic and crystalline. The crystalline state is defined as a homogeneous molecular order, throughout the system, so called remote order. Polymers, however, often only show order in two dimensions, and most fibres only order along the fibre axis. (Nationalencyklopedin, 2013-IV)

The amorphous state is defined as having a non-crystalline molecular structure, with little remote order, but has some order in its proximity. Specifically with polymers is it an unordered pattern of long molecule chains. The amorphous state has a higher energy than the crystalline, and is metastable so it strives to reach the crystalline state due its more favourable thermodynamics. In polymers, chains can bind to other chains, which greatly affect the physical properties. (Nationalencyklopedin, 2013-I)

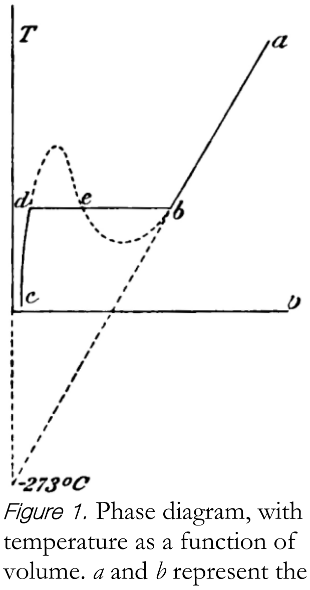

Figure 1. Phase diagram, with temperature as a function of volume. *a* and *b* represent the gaseous phase, *b* and *d* is the phase transition, *d* and *e* is the liquid phase, whereas *b* and *e* and *e* and *d* via dotted lines are the metastable regions. (Ostwald, 1897)

Being metastable means that it is to be in the transition between amorphous and crystalline states, meaning that it is unable to stop or revert the process when started. A metastable substance is labile. The change into a labile state is not instantaneous, and can be visualised with a phase diagram (see figure 1) where it represents a heterogeneous phase transition. (Ostwald, 1897)

The crystalline state in polymers is categorised with order in two of the three space dimensions, where the fibres are only ordered on the so called fibre axis. (Nationalencyklopedin, 2013-IV)

Substances, such as liquid crystals, physical property can be divided into both isotropic and anisotropic, where the isotropic means it is ordered in all directions, while anisotropic mean it is ordered in some directions.

(NATIONALENCYKLOPEDIN, 2013-II) Anisotropic materials cannot be described with a cubic crystal system, to explain how different parts are joined and interact. Cubic crystals, such as some minerals and some metallic crystals, are generally called isotropic since they can show an order in all three space dimensions, which cannot be said of polymers in the crystalline state. (NATIONALENCYKLOPEDIN, 2013-IV)

Glass transition is when an amorphous polymer goes from a glossy state to a rubbery state, with the hardness and stiffness dramatically decreasing. This is because that the molecule chains have at a certain temperature, the glass temperature, left its fixed positions and are moving more freely. (NATIONALENCYKLOPEDIN, 2015-V)

Swelling

Swelling, or imbibition, is generally understood as a solid material absorbing a liquid solvent, without any chemical changes to the material. A swelling material may only absorb a limited amount of solvent and not surpass this limit, which is called the equilibrium, which is dependent on the chemical nature of the swelling material, as well as the solvent's, the cohesion and elasticity of the swelling material, of the temperature and of the frictional forces within the solvent. (HOFMEISTER, 1890)

It is relevant to distinguish between three different kinds of swelling. The first being capillary imbibition, which is predominant in porous materials where the solvent is absorbed and the surface tension is the driving force. The second, osmotic imbibition, is found in porous material such as membranes and organic tissues, and where the osmotic force drives the swelling. The third, molecular imbibition, is found in non-porous materials and is driven by chemical forces and thermodynamics. (HOFMEISTER, 1890)

Models for the kinetics of swelling for gels and polymers

Two relevant models are the time-dependent model and the Hofmeister model. The first is for general use of polymers, while the latter was originally made for agar and glue, but intended as a general model for swelling of gels.

For the sake of convenience are the variables for the mass of imbibed solvent (W) and time (t) changed to be the same for all models, regardless of how they were assigned by its author, to make comparisons easier. Other model specific parameters and constants will be defined as they occur.

Table 1. Different transport modes for the time-dependent model. (BARTON, 1991)

$n = ½$	Case I / Fick's law. The diffusion of solvent is much less than the relaxation of the polymer.
$n = 1$	Case II. The diffusion of solvent is very rapid compared to the relaxation process.
$½ < n < 1$	Case III. Non-Fickian and anomalous diffusion. The relaxation and diffusion processes are comparable.

General time-dependent model for swelling polymers

As the name indicates is this model (see eq. 1), mostly used for polymers and to describe their swelling and the relaxation process of the gel. The amount of water imbibed is determined by the adsorption speed (k) and the transport mode (n). The transport mode (see table 1) defines what kinds of mechanism that acts upon the film. (BARTON, 1991)

$$W = kt^n \qquad \text{(Eq. 1)}$$

The Hofmeister model

The model (see eq. 2 & 3) was formulated by Hofmeister (1890) when he researched salt solutions and how they affected the swelling process of protein gels such as agar-agar and protein based glue, due to their impact on the solvent. The results would later be known as the Hofmeister series. The formula Hofmeister constructed took several physical parameters into account and had the ambition to describe the physical mechanisms that happens inside the gel as it swells.

$$W = P\left(1 - \frac{1}{1 + \frac{c}{d}t}\right) \quad \text{(Eq. 2)}$$

P is the maximum amount of solvent that the gel can absorb.
c is a gel and solvent specific constant.
d is the average thickness of gel when swollen to its maximum.

$$\frac{dW}{dt} = \frac{P\frac{c}{d}}{\left(1 + \frac{c}{d}t\right)^2} \quad \text{(Ep. 3)}$$

Gelatine

Gelatine (see figure 2) is essentially made up of proteins, and is made from the connective protein collagen. Collagen contains approximately 1/3 glycine, and is also rich in proline. It is one of few proteins containing hydroxyproline, but it lacks the essential amino acid tryptophan. Since collagen is largely hydrophilic, its secondary structure does not favour formation of α-helix chains. The tertiary structure has large scale folding and helicity. A subunit in collagen is the tropocollagen, which is a superhelix, with a repeat unit after each 100 Å consisting of three strands. These strands can be bound to other strands. (Arvanitoyannis, 2002)

The primary structure of gelatine is almost identical to collagen. The degree of maintenance of the other structures depends on melting process and extraction process. Gelatine chains may be intertwined back into the collagen helix. (Arvanitoyannis, 2002) Gelatine has a typical molecular weight of $2.0 \cdot 10^4$ to $2.4 \cdot 10^5$ Da, with an average weight of $8 \cdot 10^4$ Da. (Larsson, 1995)

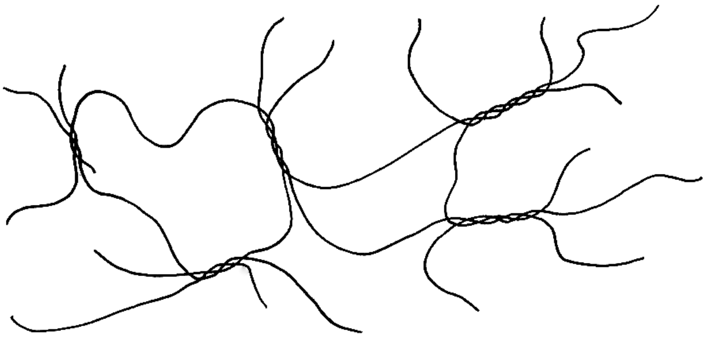

Figure 2. Illustration of a gelatine gel network, showing the peptide strands and where the triple-helix parts connect the strands. (Larsson, 1995)

Swelling properties of gelatine

Gelatine films are made from gelatine gels that have been dried. The gelatine films can be either amorphous or crystalline, which depends greatly on at what temperature the gel was produced and dried, so called 'hot' and 'cold' dried gels. Gels that are set under NTP conditions (i.e. 21 °C, 1 atm) are considered to be 'cold' dried. The swelling behaviour of gelatine films in 20 °C water, are known to be dependent on the drying temperature, which should not be so high as it destroys both the crystalline structure and non-covalent bonds. (Robinson, 1964)

The swelling of gelatine is generally considered to be due to osmotic pressure, in particular in the Procter-Wilson-Loeb theory, where the Gibbs-Donnan effect is used to explain the swelling. However, since gelatine grains at the isoelectric point of pH 4.7 does indeed swell considerable, cannot this be the only mechanism. Chemical attraction between the protein strands and the solvent is one possibility. (LOEB, 1922) The Procter-Wilson-Loeb theory was later abandoned by the scientific community.

Gelatine swelling is anisotropic, which in effect leads to that the surface area is constant. The swelling consists of an amorphous phase, a mesophase and a crystalline phase. The diffusion path is not altered during swelling, and seems independent of thickness of the film. (SHEPARD, 1923) Gelatine's equilibrium is temperature dependent and increases with temperature. If a gel has reached equilibrium and the temperature is increased it starts to swell again, but if the temperature is lowered the gel neither swell nor lose any of the absorbed solvent. (SHREVE, 1919)

The imbibition into the amorphous regions of the film, is fast because of its lower density, giving high initial swelling rates and high equilibrium uptakes. Imbibition into the crystalline regions of the film is slower and limited because they are more tightly ordered and have a higher density. Regarding swelling equilibrium it is considerable less extensive in crystalline regions than that of amorphous regions, due to the regular arrangement of polymer chains and its interactions in crystalline gelatine. Ofner argues that the amorphous region of his gels (15-25 wt% gelatine) was between 0 and 4 hours swelling, and the crystalline appeared after between 6 and 10 hours of swelling. (OFNER, 1986) The one directional swelling has the same behaviour even if the gelatine is swollen in form of beads instead of slabs or films. (KLECH, 1989)

Modelling of the kinetics of swelling for gelatine

There are several different models for predicting the swelling behaviour of gelatine films as a function of time. The most frequently used is Robinson-Ofner's empirical model, or a derivate thereof, for swelling in one direction. The formula that has some theoretical basis is the time-dependent model. The Hofmeister model was to some interest for gelatine swelling until the 1920's when it was abandoned and dismissed due to lack of empirical data supporting its validity for water with low concentrations of salt or using distilled water as solvent for gelatine. (SHEPARD, 1923)

As will be shown in the discussion of this thesis, the Hofmeister and Robinson-Ofner models do have a great deal of similarities. This is not unexpected since they are both based on empirical observation.

The time-dependent model has a very broad area of application, so it also been used to some moderate extent for predicting the swelling behaviour of gelatine (LEE, 2005).

The Robinson-Ofner pseudo-second order model

The model was first conceived by Robinson (ROBINSON, 1964) (see eq. 4 & 5), and the intense studies by Ofner (OFNER, 1986; OFNER, 1987) on gelatine gave its current form (see eq. 6 & 7). It does not claim to have any physical explanation for the swelling, and is based entirely on empirical data. Robinson's original formula differs slightly from other models since it use increase in film thickness (ΔT) due to absorption of solvent than in increase of mass solvent (W), and he assumes that eq. 5 is a reasonable assumption when deducing eq. 4. Due to gelatine's anisotropic nature there is a linear correlation between increase of thickness and mass increase due to adsorption of solvent, an assumption also Robinson did. Hence, shall they be treated as the same model.

The model generally gives an r^2 of 0.98 to 0.99 when fitted to a complete set of data for thicker gels (OFNER,1986), despite being derived for thin photographic films. However, Ofner recommends a curve fitting for the first four hours, and then another for the entire set of data. The first should be used for short-term swelling predictions, and the latter for long-term swelling predictions. This, according to Ofner, is because there are two parallel processes in swelling of semi-crystalline polymers in general, and thus effectively giving the model four variables (A_1, A_2, B_1, B_2).

$$\frac{t}{\Delta T} = a + bt \qquad \text{(Eq. 4)}$$

$$\frac{dW}{dt} = k\left(W_\infty - W\right)^2 \qquad \text{(Eq. 5)}$$

a and b are gel and solvent specific constants.
k is a gel and solvent specific constant.
W_∞ is the mass of imbibed water at equilibrium.

$$\frac{t}{W} = A + Bt \qquad \text{(Eq. 6)}$$

$$\frac{dW}{dt} = \frac{A}{\left(A + Bt\right)^2} \qquad \text{(Eq. 7)}$$

$1/B = W_\infty$ is the maximum uptake as shown in experiments. $A \propto H$, where H is the initial thickness of the non-swollen film.

Both Robinson (ROBINSON, 1964) and Ofner (OFNER, 1987) came to the conclusion that that the formula works also for additives to the thin film. In Robinson's case with silver halides, specifically silver bromide, which is found in photographic film and Ofner with various organic molecules typically found in the pharmaceutical industry, such as Octoxynol-9, dicloxacillin and others.

Introduction to Rheology

Rheology is the science of deformation and flow of matter and rheological studies are used to characterise materials, via its flow or by deformation. When used to characterise the material, it is described in terms such as viscous, elastic or viscoelastic. (BYLUND, 2003)

Viscous fluid is usually the description given to gases and liquids. The ideal viscous fluid is unable to retain any deformation energy, therefore irreversibly deformed when stress is applied. Hence it flows and the deformation energy is converted into heat energy. (BYLUND, 2003)

Elastic materials, on the other hand, are solids, and contrary the ideal elastic material stores all its deformation within, and will recover when the stress is no longer applied to the material. In this sense, can a viscous fluid be described as a fluid that resists the act of deformation rather than the state of deformation. Therefore does the elastic material refrain from both the act and the state of deformation. (BYLUND, 2003)

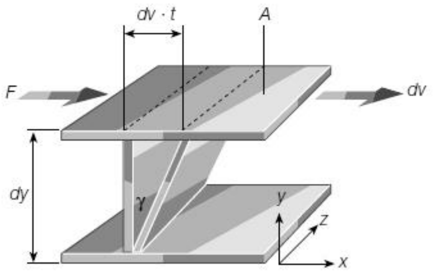

Figure 3. Shearing with two plates (BYLUND, 2003)

Viscoelastic materials, are such that have both elastic and viscous properties, in the sense that they are able to store some of the deformation energy within their molecular structure, as well some is lost by flow. Many food materials are viscoelastic (BYLUND, 2003)

The shearing of a material is the foundation of rheology, since it tells about both flow behaviour and structure. A sheared flow can be achieved with two parallel plates (see figure 3), and to study the viscosity of a material a stationary flow must be induced, and will cause a reordering and deformation of the inner of the material. The shearing between two parallel planes are used to define the concepts of shear stress and shear rate, which quantifies how much and how fast something is deformed. (Bylund, 2003)

The shear stress (see eq. 8) represents the applied force relative to the sample area. The shear rate (see eq. 9), also called shear strain, represents the displacement of the top plate compared to the sample height. From both these concepts is the apparent viscosity (see eq. 10) derived.

$$\sigma_{xy} = \frac{F}{A} \qquad \text{(Eq. 8)}$$

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{dv}{dy} \qquad \text{(Eq. 9)}$$

$$\eta_a = \frac{\sigma}{\dot{\gamma}} \qquad \text{(Eq. 10)}$$

(Bylund, 2003; Rubenstein, 2002)

Dynamic mechanical analysis

To determine the chemical composition and physical structure, is oscillatory analysis suitable for the job, including measuring gel strength, monitoring gelatinisation and glass point transition phenomenon. The setup can vary from two parallel plates (see figure 4), cone and plate to concentric cylinders. (Steffe, 1996)

A subcategory to oscillatory tests are dynamic tests, which may test stress by fixing deformation i.e. strain, and may also test deformation by fixing the stress amplitude. In the test are the materials subject to either deformation or stress, which varies over time to give a profile over the matter tested. It has been suggested that stress sweeps of the two mentioned give superior results, however the frequency sweep is the most common mode of testing, since it shows the viscous and elastic behaviour and how they change with the rate of strain. Several assumptions are made for the mathematical models, including that strain is the uniform over the gel, that sample inertia can be neglected, and that the material behaves as a linear viscoelastic substance. (Steffe, 1996)

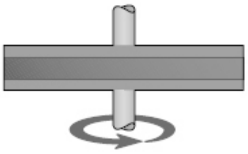

Figure 4. Plate-plate setup, with sample sandwiched between two plates. (Bylund, 2003)

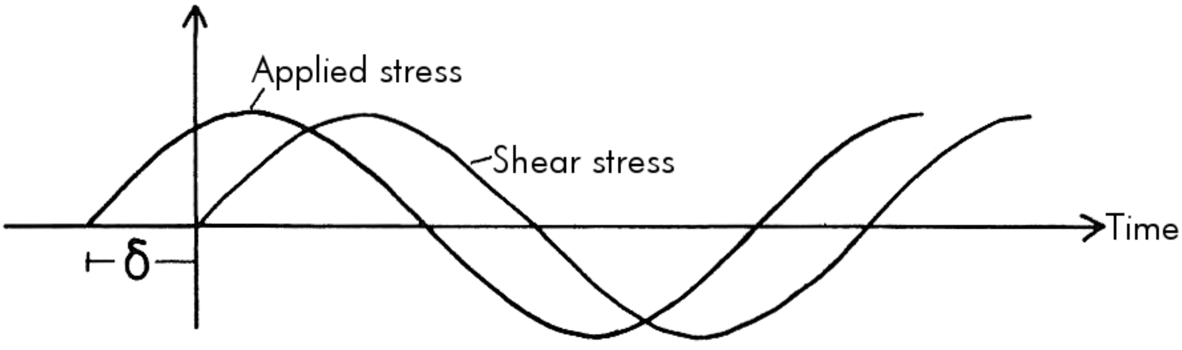

Figure 5. Difference between input and material response with dynamic mechanical analysis. (Larsson, 1995)

The shear storage modulus (sometimes called elastic modulus, see eq. 11) and shear loss modulus (viscous modulus, see eq. 12) are measured. Together they form the complex modulus (see eq. 13). However, most literature prefer to call the length of G for complex modulus (see eq. 14) despite it being a real figure and not complex.

$$G' = \frac{\sigma_0}{\gamma_0}\cos\delta \qquad \text{(Eq. 11)}$$

$$G'' = \frac{\sigma_0}{\gamma_0}\sin\delta \qquad \text{(Eq. 12)}$$

$$G = G' + iG'' \qquad \text{(Eq. 13)}$$

$$G^* = \frac{\sigma_0}{\gamma_0} = \sqrt{(G')^2 + (G'')^2} \qquad \text{(Eq. 14)}$$

σ_0 is the amplitude of shear stress
γ_0 is the maximum strain
δ is the phase shift relative to the strain input on the material.

(STEFFE, 1996; RUBENSTEIN, 2002)

Another relevant measurement is the tangent of the phase angle (see eq. 15), which describes the viscoelastic behaviour and is a function of the frequency. This value is very high for dilute solutions, about 0.2 and 0.3 for amorphous polymers and low, in the range of 10^{-2}, for glassy crystalline polymers and gels.

$$\tan\delta = \frac{G''}{G'} \qquad \text{(Eq. 15)}$$

(STEFFE, 1996)

Fluid dynamic gauging (FDG)

FDG is a non-invasive technique to measure the proximity of a surface. The method was developed at the Department of Chemical Engineering and Biotechnology at the University of Cambridge to measure the thickness of deposits in-situ and online. FDG measures the thickness of films, such as fouling deposits, with a nozzle that gauges the surrounding solvent. Depending on the flux through the nozzle of the solvent can the distance from the nozzle to the surface be estimated through a calibration curve, in which known distances from the surface correspond to a measured flux. (WILSON, 2000)

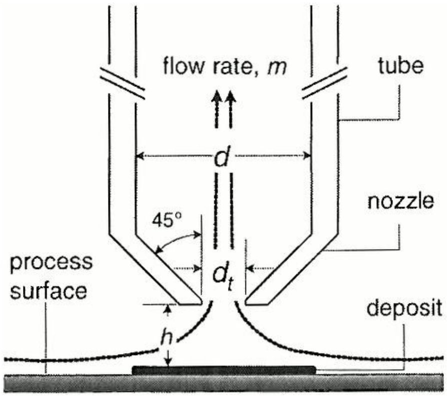

Figure 6. Illustration of FDG nozzle and film. (CHEW, 2006)

Especially within food technology and biotechnology it is often problematic to examine films and deposits outside its natural environment, either it is too brittle to be removed or too soft to use traditional measurements. The material might shrink or slump when removed from its environment, hence a need to measure it in-situ. The method is also well suited to work in sterile environments or where there is a risk of contamination when introducing foreign objects. (WILSON, 2000)

Solvent will be sucked via a nozzle from the surroundings of the film (see figure 6). The core principle is that he flow rate (m) of solvent will vary with the distance (h) to the film, i.e. $m \propto h$. Note that the flow rate also depends on the properties of the solvent, the hydrostatic head and the height of the nozzle above the film, i.e. $m(\rho_{solvent}, \mu_{solvent}, s, h)$. Measuring the flow rate will give the distance to the film, and knowing the distance to the process surface, will give a measurement of the deposit's thickness within 20μm accuracy. (WILSON, 2000)

In a FDG-rig (see figure 7) is the driving force is the hydrostatic head (*s*) which is created with a siphon effect, hence no need for pumps or such. With a greater hydrostatic head the greater will the suction of solvent be due to equation 16. (Wilson, 2000)

$$\Delta p = \rho g s \qquad \text{(Eq. 16)}$$

$$\frac{h}{d_t} < \frac{1}{4} \qquad \text{(Eq. 17)} \qquad \text{(Wilson, 2000)}$$

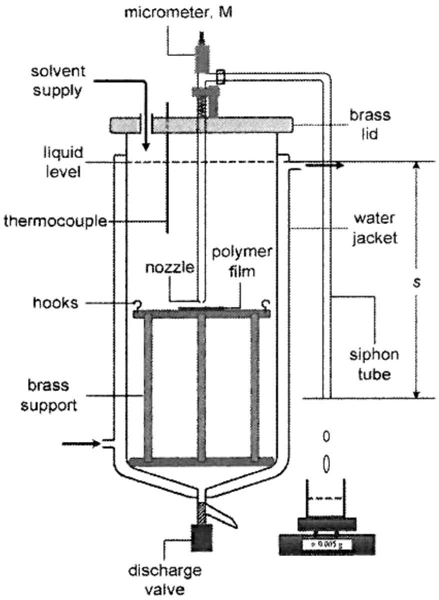

Figure 7. Illustration of a FDG-rig with water jacket for controlling solvent temperature. (Chew, 2006)

Due to that the flow through the nozzle is laminar and that the solvent is an incompressible Newtonian fluid, should equation 17 be fulfilled to be able to acquire accurate measurements, according to empiricism but also due to the Haugen-Poiseuille equation when trying to calculate the discharge coefficients. (Chew, 2006; Wilson, 2000) When the nozzle is this close to the surface, it is called to be in the incremental zone and when the nozzle is further beyond it is in the asymptotic zone. However, if the nozzle is too close to the surface (i.e. $h << d_t$) it will result in a radial flow like a turbine due to the nozzle's cylindrical geometry and might damage the deposit. (Wilson, 2000)

MATERIAL

Commercial gelatine leafs, Marks and Spencer (84 % protein, batch 9026), and food colouring agent E124 was used in all swelling experiments.

Fluid Dynamic Gauge rig, which was constructed by the Department of Biotechnology and Chemical engineering at the University of Cambridge.

Water, purified with reverse osmosis filter.

Circular stainless steel plates with the diameter of 50.0 mm, manufactured at the Department of Biotechnology and Chemical engineering at the University of Cambridge.

Chemically pure acetone was used to clean the stainless steel plates.

Electronic scales, Precisa XB3200C & Precisa XB120A, which were used to measure the weight increase of the swollen gels. Different scales were used depending on needed accuracy.

Bohlin CVO, for measuring rheological properties of the gel.

Perkin Elmer, Differential Scanning Calorimeter – Pyris 1, for measuring the glass transition point.

Mathworks Matlab 2013a, was used for processing data and make calculations with it.

A Casio fx-82D Fraction and fx-82 Solar Fraction scientific calculator were used for intermediate calculations, especially in the lab.

Haake Fisons C1 water heater with custom made gas-liquid heat exchanger, was used to control the temperature of the experiments.

Digital callipers, was used to measure the thickness of dried film.

Digital stopwatch, was used to assist measurements with the Fluid Dynamic Gauge rig.

METHODS

The methods of the experiments can be summarised into steps: making the gel, measuring solvent uptake via the gravimetric method (A) or via FDG (B), as illustrated in figure 8. Analysing the physical properties of the gel can beneficially be done during some of the stages of the making of the gel.

Figure 8. Flowchart of the different experiments.

Preparation of gelatine samples

- Soak 5.95 g of Marks & Spencer gelatine leafs (84 % protein, batch 9026) in 100 ml of room temperate reverse osmosis water. Soak them for at least 10 minutes, as recommended on the package.
- Heat the water with the leafs while steering on low heat (<50 °C). When it has melted completely and no protein strands can be visually observed in the liquid, add a drop of food colouring (E124).
- Add 5.00 ml of gelatine liquid on top of a stainless steel disc with a diameter of 50 mm in a petri dish. The 5.00 ml is the casting volume of the gel. The stainless steel discs have been cleaned, first scrubbed thoroughly and then soaked in acetone for a minimum of 1½ hours. If the discs have not been scrubbed thoroughly enough they will be covered with a film after the acetone-bath. Apply the liquid on stainless steel plates that have been taken directly from the acetone-bath, after the acetone has evaporated. Do not touch the edges or the top, touch the underneath of the disc when moving it.
- Let the films set at cold temperature (about 3 °C) for 5 minutes or at room temperature for 30 minutes. When producing thicker films (about 5 ml or more of gelatine solution) should let to be set in room temperature, since the surface easily can be disturbed and the liquid gelatine run off the discs.
- Let the films dry in front of an air conditioner, so the drying velocity surpasses 0.24 g solvent/hour, hence avoid the formation of air bubbles inside the dry gel. After 24 hours has the drying process stopped, and will not lose any more solvent.
- Store the films in the cold room for future use. Please see chapter on discussion of drying films.

Optimising drying speed of gelatine films

A tray with eight discs with newly made films, according to the protocol above, was left in a droughty area nearby the outlet of an air-conditioner (see figure 9). The plate was situated so the airflow went through a slit, hence diversified the airflow due to Bernoulli's effect, and as a result the air convection over the different samples was different for different sampled, depending on their proximity to the slit.

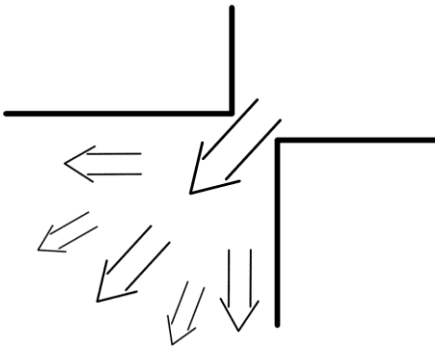

Figure 9. Illustration of drag from air-condition facility and Bernoulli's effect.

Swelling experiments

As stated in the aims, is the main purpose to study the kinetics of swelling for gelatine. This can be done with different methods of measurement. Either to measure the imbibed solvent in the film, method A, or to measure the thickness increase of the film, method B. Both methods are well established within the field of gelatine swelling, and given that the swelling of gelatine is anisotropic (SHREVE, 1919; SHEPARD, 1923; ROBINSON, 1964; OFNER 1986) they ought to give the same results.

Two parameters that were investigated are: the casting volume of the gel, i.e. indirectly the initial film thickness (the gels are assumed to dry to the same level of dryness) and the temperature of the solvent (see table 2). The surface area was kept constant at 19.63 cm^3 (the discs were circular and had a diameter of 50 mm).

Table 2. Table over performed swelling experiments. With method A was all experiments performed. With method B, just those with 5.00 ml as initial volume. Showing which casting volumes that has been allowed to swell at what temperature.

21.0 °C	1.8 ml	4.2 ml	5.00 ml	7.2 ml
25.5 °C			5.00 ml	
27.5 °C			5.00 ml	
31.0 °C			5.00 ml	

Method A – Gravimetric measurements

Method A measured the weight of the imbibed solvent in the swelling gel, i.e. how much the solvent inside the gel weighed.

The underlying idea with the experiment was to make it a fairly straight forward experiment where the execution of it would be uncomplicated and the experiment easy to repeat, and therefore make it as insensitive to the choice of operator as possible. The experiment protocol is original for this particular project. Due to the simplicity of the experiment design, was it easy to have several films (at 21 °C, 3 films) swelling parallel which resulted in more accurate measurements. At temperatures above 21 °C were a 2x2 film setup used where two films were swollen at one occasion and then two more from the same batch at a different occasion, usually the day after. This was due to the limited space in the heated water bath (Haake Fisons C1).

The experiment measures how much of the solvent has been imbibed into the swelling gel. However, this is only measured indirectly. It is necessary to know the initial dry weight, from which the amount of gelatine solids can be calculated. Also, the surface layer of non-imbibed solvent must be considered as well. After the experiment has been completed is it necessary to weigh the stainless steel discs on which the film was attached to.

Solvent imbibed into film = Measurement – Mass of disc – Mass of solid gelatine – Mass of surface layer of solvent

Experiment

A disc with a gelatine film was weighed before the experiment to acquire an initial dry weight. The disc was then lowered into the solvent and taken up after a few seconds. The disc was slightly tilted (approx. 30°) and then gently tapped towards the edge of the beaker in order to minimise any surplus solvent residing on top of the film, then wiping the underneath of the disc dry with a piece of paper. The disc was then weighed again to acquire an estimate of how much water was associated with the surface of the gelatine film due to the surface tension, i.e. the amount of water that is not imbibed into the gelatine but still electrostatically attached to the gel. When swelling the gelatine film (see figure 10) was the disc taken up from the solvent were the disc gently tapped against the edge of the beaker, the underneath wiped dry and then weighed. The film would then have been out of the solvent between 30 and 60 seconds, a period of time considerably short enough to prevent any

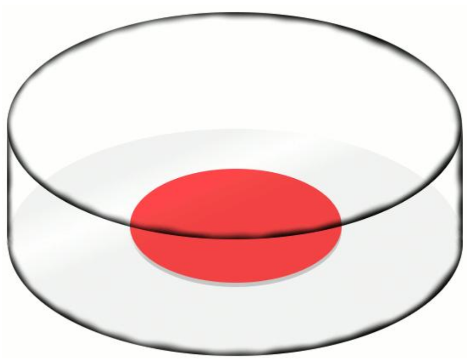

Figure 10. Disc with gelatine film in petri dish.

drying between swellings. The time the film spends in the solvent was kept with a digital stopwatch. After the experiment has been terminated the swollen gelatine film was washed off with hot water, and the disc dried off with some paper in order to be able to weigh the mass of just the disc.

The weight of both the disc and the gelatine network can reasonably be assumed to remain constant throughout the experiment. Some detachment of the gelatine gel is however to be expected, but is low in comparison to the total mass of the gel, and if the fragments are large enough to be visible they can still be picked up and weighed with the rest of the gel. It is unknown if the surface layer change as the experiment proceeds, but it is not unlikely since experiments would show if the nature of the gel changed during the experiment. Due to practical difficulties to re-estimate how much of the solvent constitute the surface layer in the middle of the experiment, it is assumed to be constant, but it is a relatively small number of typically 0.10-0.15 g solvent/film (0.005-0.008 g/cm^2). This figure should be seen in the perspective that it takes just a few minutes to gain 0.5 g solvent for a film made of 5 ml gelatine liquid, and about an hour to absorb 2 g of solvent into a typical gelatine gel.

Method B – Fluid Dynamic Gauging (FDG)

Method B measured the volume of the imbibed solvent in the swelling gel, i.e. how much the gel has increased in height. FDG (see figure 7) measures the distance to the film surface via the flux that passes through the nozzle. Knowing the distance between the nozzle and the plate, upon which the film sits, one can calculate the thickness of the film. In practice, when the thickness of a film is measured, it is necessary after the experiment has been completed to scrap off a part of the film and measure the flux again to acquire the distance to the disc that the film was attached to.

Thickness of film = Distance to film from nozzle – Distance to disc from nozzle

Calibration

An empty disc is attached and put in the tank, which is filled with the solvent, so it is situated below the nozzle. The nozzle is moved in towards the disc till it physically touch it. The nozzles height is read on a micrometer. The nozzle is then moved out as far as possible, and an undertow is created on the other end of the nozzle, which is maintained via the siphon effect. The nozzle is then moved in towards the disc again, first to a region far enough away from the film where it is assumed that the flow will be unaffected of the discs present. A measurement is taken: the liquid that is sucked up through the nozzle is collected in a beaker while a stopwatch keeps track of how long the measurement takes. The beaker is weighed and a mass flow can be calculated. The nozzle is then moved in systematically and the process is repeated till it touches the disc again. The nozzle is then moved out and measurements are done once again on the same heights above the disc as performed when moving towards the disc in order, to validate the measurement. An example of a calibration curve can be seen in figure 11.

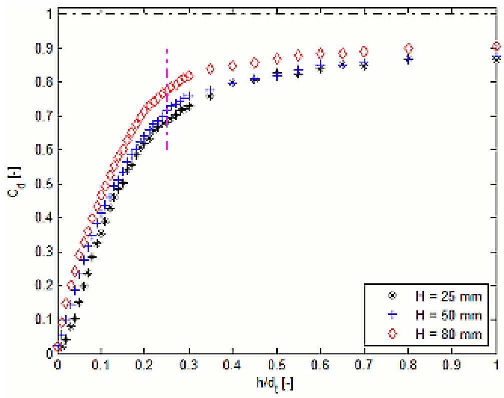

Figure 11. Example of calibration curve for an FDG-rig. The x-axis is the nozzle's height over the surface divided by the diameter of the nozzle. The y-axis is the normalised flow through the nozzle. H, the hydrostatic head, the difference in surface and drop, hence driving force.

It is important that during all time of the measurements to keep the level of the solvent constant in the tank, so the flux in and out of the tank remain the same. If the level of the solvent change, then also the driving force for the flow will change.

Experiment

A disc with a gelatine film was weighted before the experiment to acquire the initial dry weight. When the film is put in solvent a stopwatch is started to measure the total amount of time spent on swelling. There are two modes of operating the gauge rig, but the concept remains the same (see figure 12), that the solvent is sucked out near the film and the proximity to the film determines the flow out of the tank.

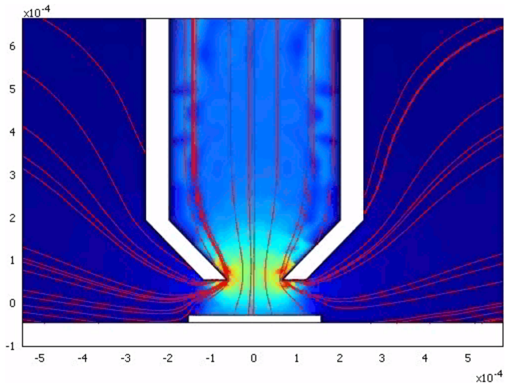

Figure 12. Detail of the nozzle of the FDG with sample.

The first mode is to keep the nozzle at the same height throughout the experiment and measure the change of flux. The flux will decrease the closer the film comes to the nozzle, or rather how much it has swollen. This might give less accurate measurements if the nozzle is too far away from the surface, due to the geometrical shape of the calibration curve. [Chew ref!] The second mode is to keep the nozzle at the same relative distance from the film. That is, if the film is swelling, then the nozzle is moved out so the flow of solvent through the nozzle is constant, hence applying the same amount of force to the film. Since the nozzle generates suction and also a pushes the film down if the nozzle is very close to the surface, it is for some materials important to control the amount of force applied through the nozzle. The force applied from flow under the nozzle may also retard swelling.

Temperature control for method A and B

The temperature in the two above mentioned experiments were controlled in an identical fashion. The experiments which were carried out in room temperature was the equipment placed next to the outlet of the air-condition facilities, which gave a measured temperature of the solvent of 21.0 ± 0.5 °C at all time.

To acquire solvent temperature above room temperature a heated water bath, a Haake Fisons C1, was used. Since the tolerance of the thermostat in the water bath was several degrees, it was not precise enough so it had to be improved. The idea was to increase the intervals with which the heater was turned on by cooling the solvent externally, so the heater would almost always be on because the solvent is continually cooled and a stable temperature equilibrium will be reached.

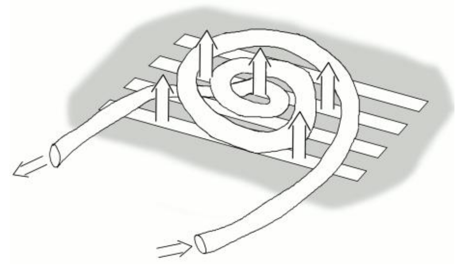

Figure 13. Improvised gas-liquid heat-exchanger, where water ran through the tube and cool air came out of the air-conditioner.

The heated solvent was re-circulated in a 2 metres long PVC-tube with the diameter of 1 cm. The PVC-tube was bent and placed on top of the outlet of the air-conditioner so the entire PVC-tube fitted over the outlet (see figure 13). The air-conditioner was set to approximately 15 °C on a typical English summer day. The measured variance in the water bath was 0.3 °C in the temperature interval 25 to 31 °C. In the case of the FDG experiment the heating liquid was first pumped into a heating-jacket around the rig (see figure 7) before it was sent through the 2 metres long PVC-tube.

Analysis

Density measurements of different gelatine states

Gelatine exists in various forms, such as liquid solution, solid amorphous and as gel. For various calculations it was important to know the density of gelatine, both as solution and in the brittle amorphous form. The densities were particularly needed for the mass measurements.

Liquid gelatine solution

When making the films the stainless steel disc set-up was placed on a scale where the known volume of liquid gelatine solution was applied. Since about 8-10 discs with gelatine were usually made each time, a good average can be obtained via this method. This experiment can also be used as an indirect method to detect possible contamination in the batch.

Density = volume of liquid in pipette / weight of liquid
Density = volume of liquid in pipette / (total weight – weight of disc)

Solid amorphous gelatine film

A very thin film that had detached itself from the steel disc was used, it was assumed that the water content of the film had reached an absolute minimum, since it had the ability to dry from two directions instead of just one due to the films detachment from the steel plate, and therefore the water content was considered to be negligible. The thin film was characterised as fragile and brittle, and not at all as tough and hard as it would have been if the film was still attached to the stainless steel disc. A square of the film was cut out and its size measured. The piece of film was weighted on a high precision scale. The thickness was measured on multiple locations of the surface with a digital calliper, so a reliable average height could be calculated.

Density = (base of film piece)^2 *× average height / weight*

Calculation of volume fraction of solvent in swelling gel

The density of the swollen gelatine gel was deemed to be approximated with combining the density of the amorphous gelatine film (dry matter) and the density of solvent, since the gel would consist of mostly the solvent after it started to swell. To actually measure the density for a gel would be very bothersome since it change with solvent content and temperature.

The density of the gel was not used per se, but instead the volume fraction was is of greater interest.

Volume fraction of solvent = Volume of solvent imbibed / Total volume of gel
where the *Volume of solvent imbibed = Weight of solvent imbibed / Density of solvent*
and *Total volume of gel = Volume of solvent imbibed + Weight of amorphous gelatine / density of amorphous gelatine*

Accuracy measurements of pipettes

The accuracy of the pipettes used, as shown in figure 14, were controlled by pipetting room temperated water onto a beaker of known mass on a scale and take note of the mass reading. A 3 ml plastic pipette and a 5 ml glass pipette were controlled. The plastic pipette was controlled much more vigorously, with 21 data points each at the 2 and 3 ml readings on the pipette, to establish its actual volume. The glass pipette was only controlled with 10 data points at 5 ml, since it was designed for high accuracy measurements.

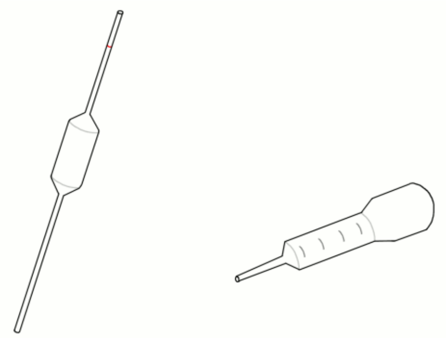

Figure 14. Illustrations of 5 ml glass pipette and 3 ml plastic pipette. NB! Not in scale.

Differential Scanning Calorimeter measurements

To determine the glass temperature (T_g), a small piece of gelatine film (approximately 50 – 100 mg) was put in a Differential Scanning Calorimeter (Perkin Elmer, Differential Scanning Calorimeter – Pyris 1) that made an automated analysis. The machine investigated the temperature span between –20 and 80 °C, with an increment of 10 °C/minute. It is praxis to use a more rapid increment, for instance 100 °C/minute, to acquire sharper and better defined curvature. But in the case with this particular material, did the water in the film generate a great deal of background noise at larger increments, hence the slower 10 °C/minute.

The experiment was designed and performed by Zlatko Saracevic, MA (Cantab), who also did the necessary calculations.

Rheology

It is important to characterise the gels to allow for comparison. A freshly set gel was put in a Bohlin CVO with a plate-plate setup (see figure4), using the rough head, which was allowed to touch the gel so it was sandwiched, before any resi-dual gel was removed. The Bohlin then performed an amplitude sweep, where the shear stress was varied from 0 to 5,000 Pa. Another gel was used to perform a frequency sweep, in an identical fashion, where the frequency was varied from 0.1 to 100 Hz with fixing the stress amplitude. The temperature was kept at 21.0 °C at all time during the experiments, via the Bohlin's internal cooling system. Increments of the independent variable were done logarithmically in both experiments.

The experiment was designed and partly performed by Dr. Joel Taylor.

Evaluation of data

All data was processed with Mathworks Matlab, especially when performing non-linear curve fitting, which utilise the least square method. To some extent was also a scientific calculator used.

Data from measurements for Method A, where more than one sample was used most often a set of three or four, was data for each point in time averaged. This was done to minimise abnormal readings and operator induced errors. Data from Method B was not, since FDG equipment only allowed for one sample at the time to be examined. Also, moving around the samples in the FDG would most likely generate operator induced measurement errors, since the sample must be in the same position to have micrometre precision.

All experiments were single experiments, since there was not enough time to repeat them.

RESULTS

Swelling

The kinetics of swelling was measured with two different methods, the gravimetric method and the FDG.

Method A – Gravimetric Measurements

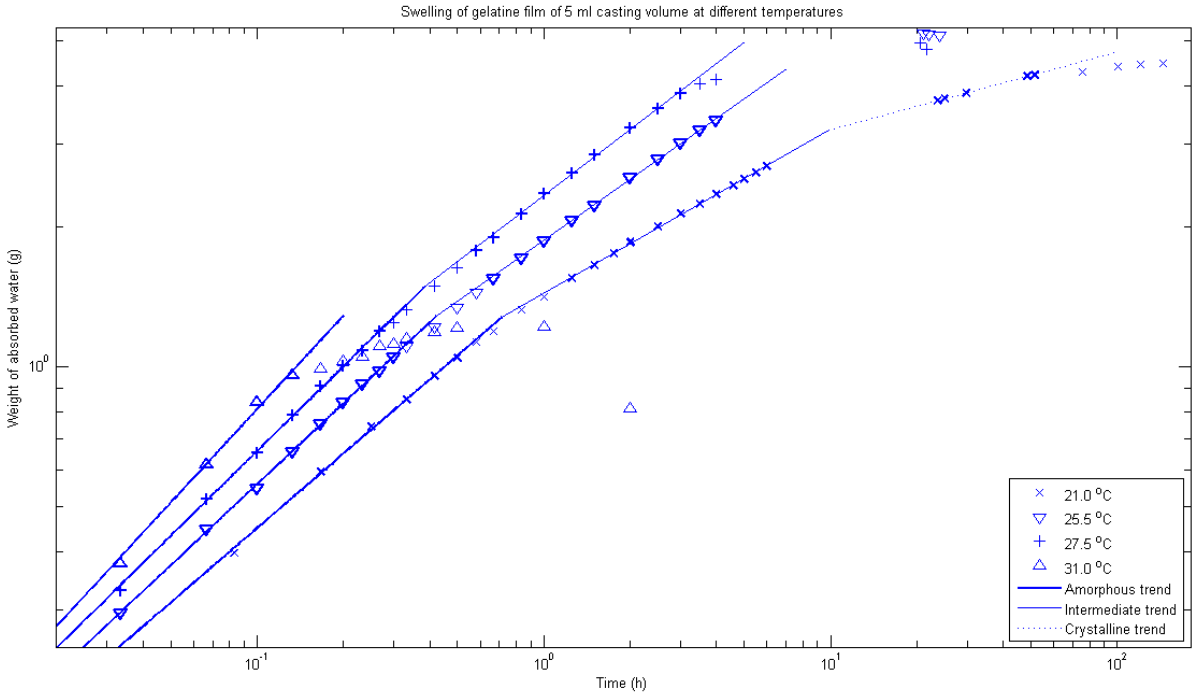

Figure 15. Swelling of gelatine films at different temperatures, where earliest measurements were taken at 2 minutes after the swelling has started. Marked points were used for fitting the lines.

As stated in table 2 and can be observed in figures 15 and 16, the experiments were carried out in such a fashion that both the initial thickness of the films and the temperature varied. Where the temperature was varied the initial thickness of the films was kept constant as they were made from 5.00 ml 4.7% gelatine solution, as described in appendix 1. When the initial thickness was varied, this was accomplished with changing the volume of 4.7% gelatine solution when making the gels, but all of these experiments were performed at the same temperature, 21 °C.

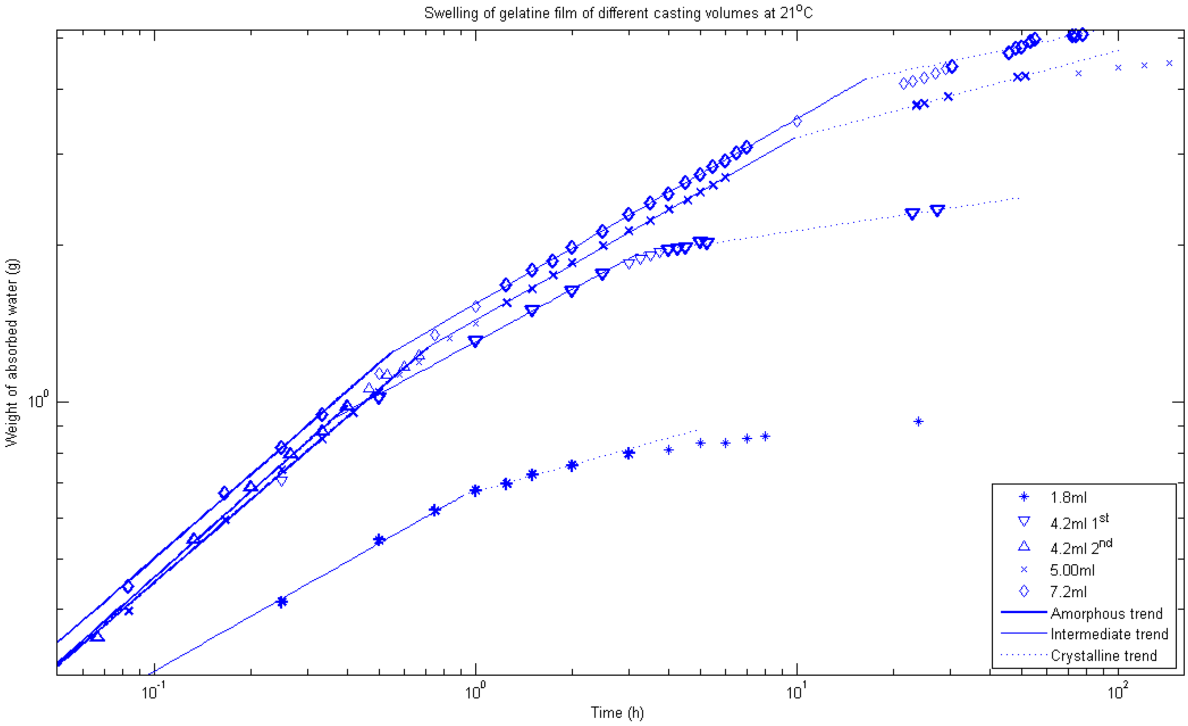

Figure 16. Swelling of gelatine films of different thicknesses at the same temperature, where earliest measurements were taken at 1 minute after the swelling has started. Marked points were used for fitting the lines.

Method B – Fluid Dynamic Gauging (FDG)

A complete swelling of a gelatine film made from a 5.00 ml casting volume at 21 °C, were preformed while analysing it with FDG (see figure 17). Please note that the appearance of two parallel curves in figure 17, are the results of measurement errors.

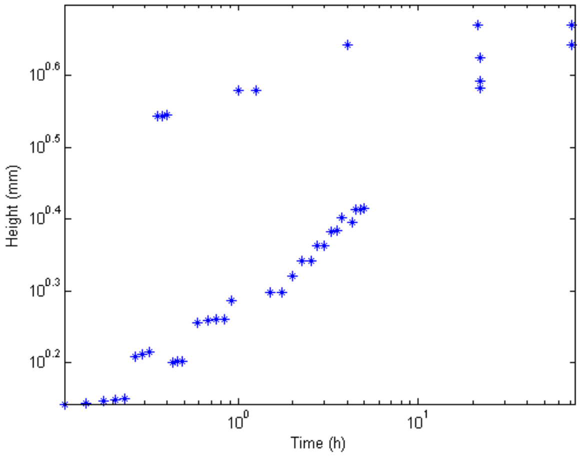

Figure 17. Swelling of a gelatine film of a casting volume of 5.00 ml. Swollen at 21 °C.

Models for kinetics of swelling for gelatine

The research performed has found two models that usually have not been used to describe the kinetics of swelling for gelatine, when investigating the existing literature. The first model is an original and empirical model, which has sigmoidal characteristics. It describes the entire swelling process, from start to the end. The second model, the time-dependent kinetic model, has primarily been used to identify the different physical states that the gel undergoes when swelling.

The Pseudo-Sigmoidal Model (PSM)

If one logarithms the time axis one notice that the data takes the clear shape of a sigmoidal curve (see figure 18).

$W = \dfrac{A}{1 + Be^{-Cx}}$ given the substitute

$x = \ln t$, which is can be written as

$$W = \frac{A}{1 + B/t^{C}} \qquad \text{(Eq. 18)}$$

$$\text{or } W = \frac{1}{A^{-1}B/t^{C} + A^{-1}} = \frac{t^{C}}{A^{-1}t^{C} + A^{-1}B}$$

The model uses three degrees of freedom instead of four, and gives a higher accuracy than the Robinson-Ofner model. This model is completely empirical, like the Robinson-Ofner and Hofmeister models.

For coefficients for the PSM see appendix II.

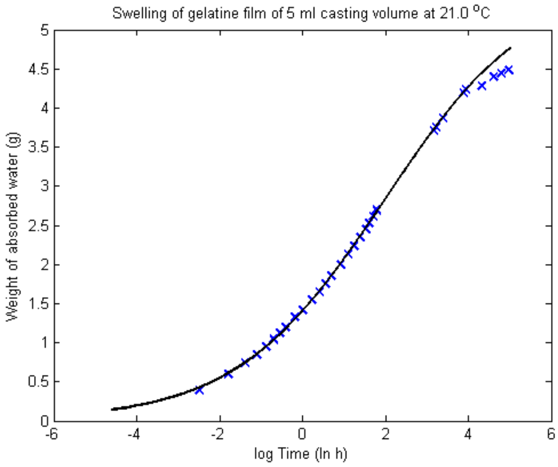

Figure 18. Demonstrating the sigmoidal shape in the swelling data swelling. Data to be found in Appendix III: Swelling dried gelatine film at 21 °C, made from 5 ml gel, gravimetric experiment.

Time-dependent model

The time-dependent model describes the amount of solvent imbibed, which is determined by the adsorption speed (k) and the transport mode (n). The transport mode (see table 1) defines what kinds of mechanism that acts upon the film. (BARTON, 1991)

$$W = kt^{n} \qquad \text{(Eq. 1)}$$

The transport modes for the amorphous and mesomorphic region are shown to be linearly dependent on temperature (see figure 19 and 20 and table 4). It is not inconceivable that also the crystalline region has a similar relationship with temperature. All regions are shown to be independent of the initial film thickness (see table 3).

The absorption speed (k) can be approximated with the Arrhenius equation. An Arrhenius (see figure 20) plot of the transport velocities given by the time-dependent model, gives that the activation energy for the amorphous region to be 970 J/mol and for the intermediate region 759 J/mol.

$$k = Ae^{-E_a/RT} \qquad \text{(Eq. 19)}$$

Table 3. Table over modes of transport (*n*) for swelling gelatine films at 21 °C. Annotation: 1. Uncertain measurements due to leaching gel.

	Casting volume		Meas. 1	Meas. 2		
Region	0.91 ml	1.82 ml	4.16 ml	4.16 ml	5.00 ml	7.17 ml
Amorphous				0.5469	0.5307	0.5356
Intermediate	0.3307	0.3506	0.3350		0.3521	0.3558
Crystalline		0.1716	0.0905 [1]		0.1666	0.1284 [1]
Reg. IV		0.0674			0.0691 [1]	

Table 4. Table showing the regions as a function of temperature for gels of 5.00 ml casting volume. Annotation: 1. Uncertain measurements due to leaching gel.

	Temperature			
Region	21 °C	25.5 °C	27.5 °C	31 °C
Amorphous	0.5307	0.5781	0.6043	0.6660
Intermediate	0.3521	0.4345	0.4705	
Crystalline	0.1666			
Reg. IV	0.0691 [1]			

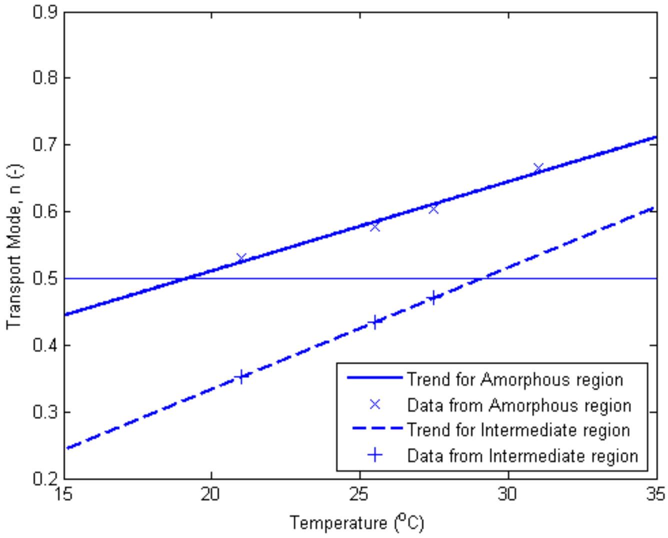

Figure 19. Plot showing a linear correlation between the transport mode and the temperature (for 5.00 ml gels). The thin line is added for comparison and represents Fickian behaviour (*n*=½).

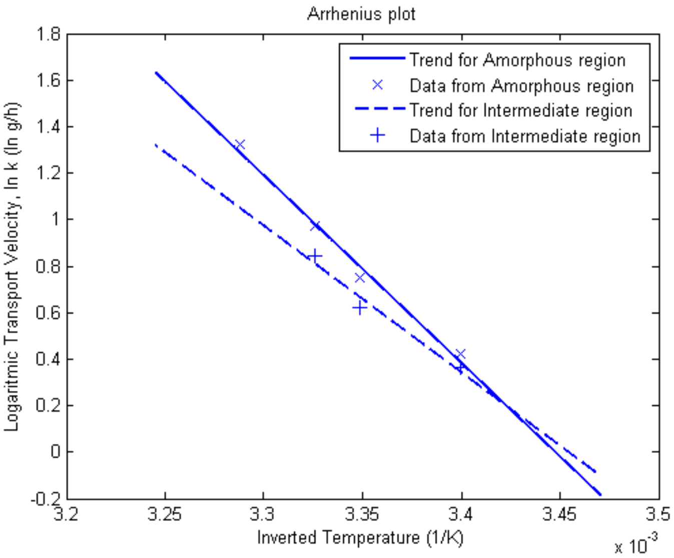

Figure 20. An Arrhenius plot with the different transport velocities given by the time dependent model for 5.00 ml gels.

Rheological Studies

Rheological studies were conducted on both a freshly made gel and a gel that has been let to swell for 12 or 13h in a Bohlin CVO, which is a machine for dynamic mechanical analysis. Both a frequency (see figure 21) and amplitude sweep (see figure 22) was done in order make comparison with other gelatine gels in the literature.

In case of the frequency sweep the gel breaks at somewhere between 10 and 40 Hz, and in the case of the amplitude sweep the gel breaks at an applied stress of approximately 1 kPa. Both the fresh and rehydrated gels express the same properties.

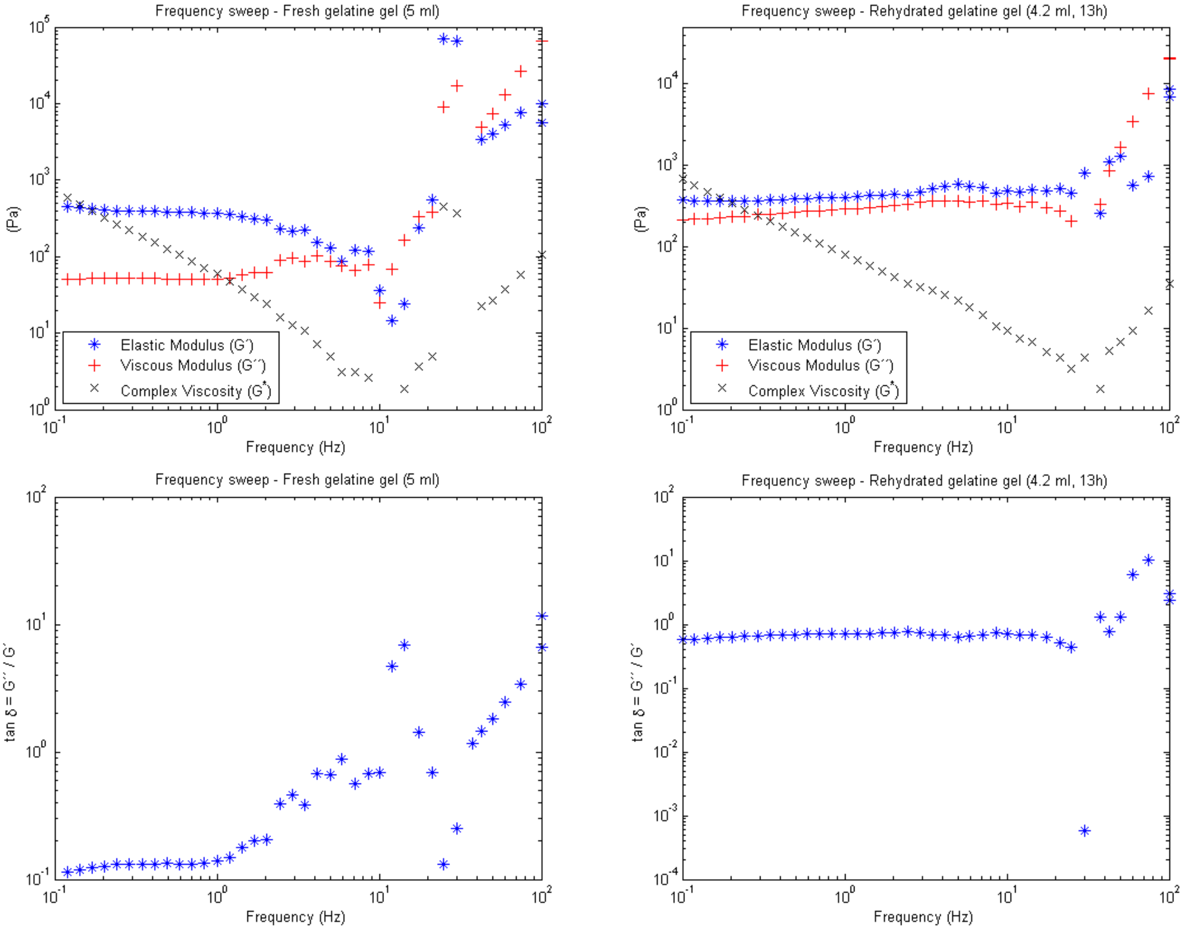

Figure 21. Dynamic mechanical analysis, frequency sweep of gelatine samples. Freshly made and rehydrated samples. The latter had swollen for 13 hours.

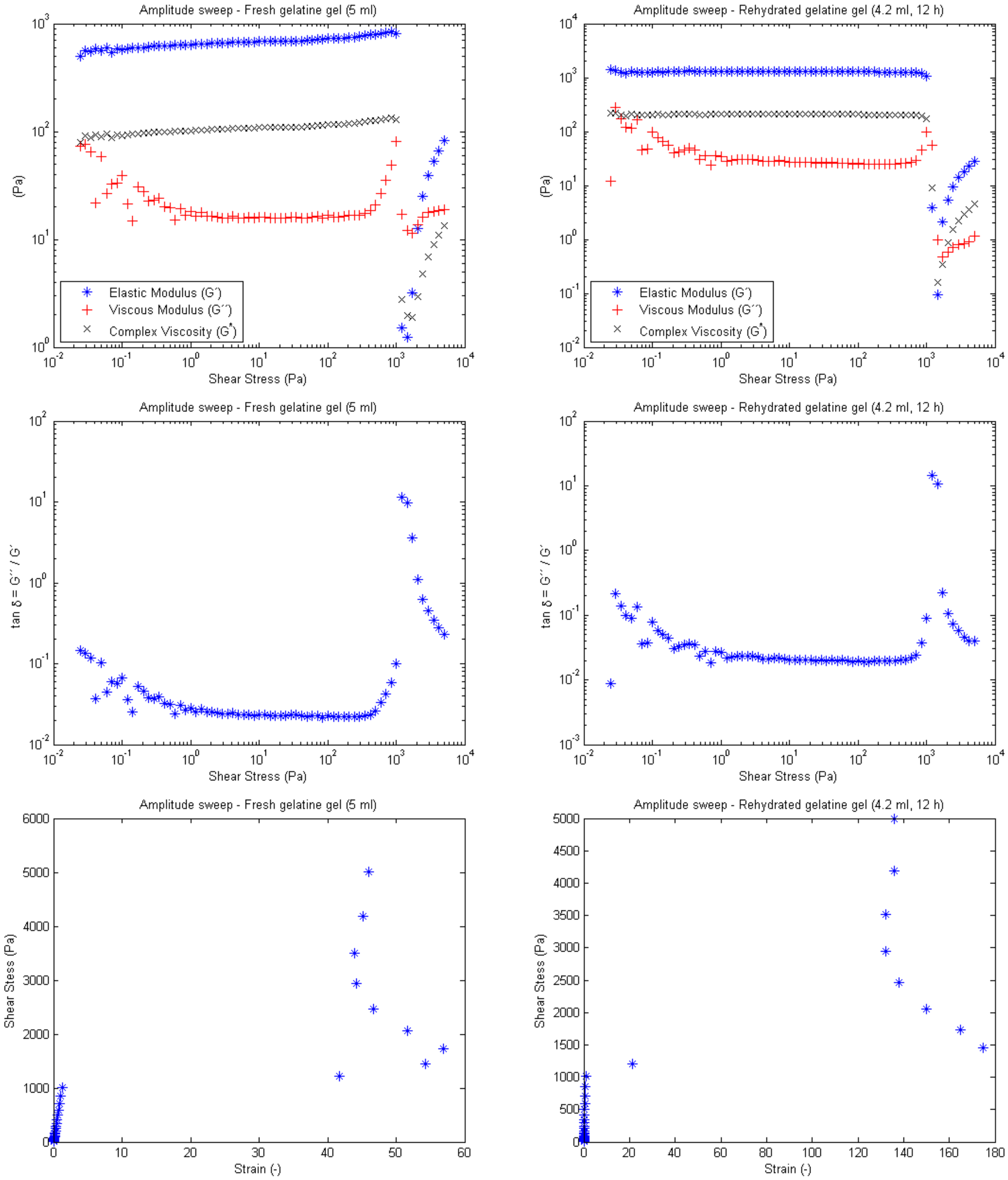

Figure 22. Dynamic mechanical analysis, amplitude sweep of gelatine sample. Freshly made and rehydrated samples. The latter had swollen for 12 hours.

Enthalpy and glass transition point measurements

The glass transition point (see figure 23) were determined via the usage of Differential Scanning Calorimeter (DSC), and the transition starts at 28.25 °C and has stopped at 28.75 °C.

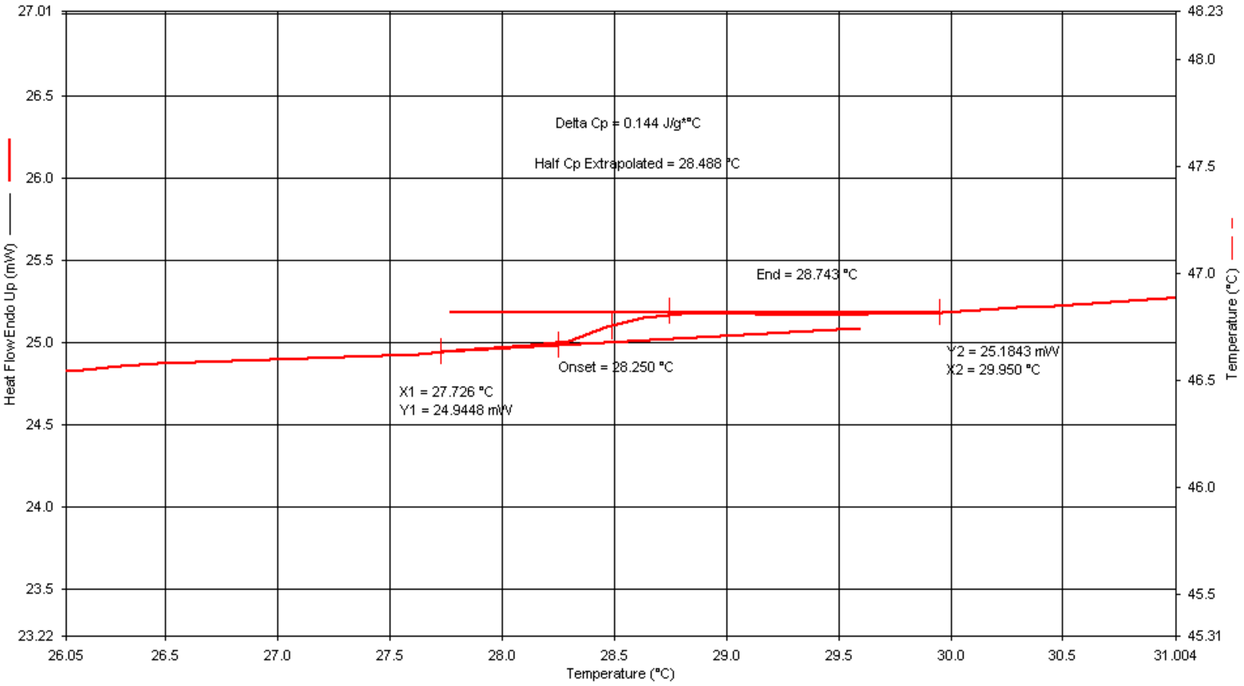

Figure 23. DSC measurements of freshly made gelatine gel.

Density measurements

Solid amorphous gelatine film

Density of gelatine film made according to protocol (see Appendix I & III)

$$\rho_{film} = 1274 kg/m^3$$

Density of the raw material, sheets from Marks & Spencer (see Appendix III)

$$\rho_{M\&S} = 1291 kg/m^3$$

Liquid gelatine solution

$$\rho_{solution} = 975 kg/m^3$$

Optimisation of drying procedure

The optimisation of the drying gave some interesting results, as it appears that there is a lower limit on how slow the gels might dry. The samples closest to the slit (see figure 9) had the highest convection, on average 0.25 g/h, and those furthest away had the lowest (see figure 24). There are two different stages of the drying and both appear to be approximated with a quadratic curve each.

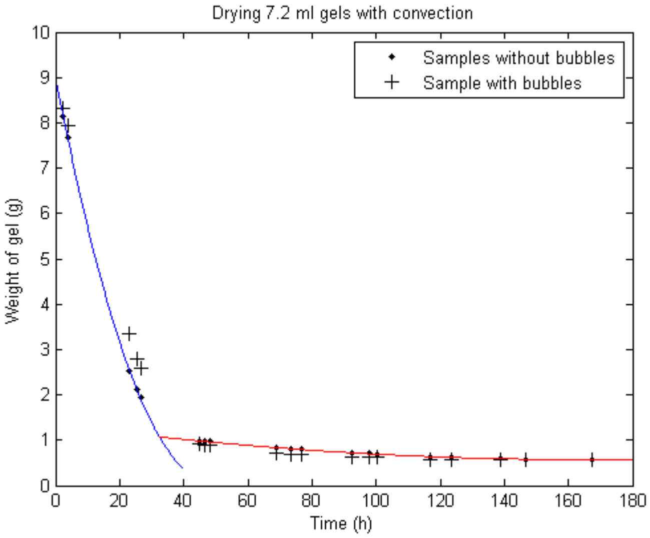

Figure 24. Drying curve of a thick gel that is exposed to various degrees of convection. Comparing the samples that did with those that did not form bubbles during drying.

DISCUSSION

Experiments

One of the weaknesses of method B, the FDG method, is that it is sensitive to whom is operating the rig, since it demands that certain parts of the measuring procedure is done very consistently. This might induce a systematic error. A computerised version of the FDG rig has therefore been manufactured in order to eliminate the operator factor from the statistic uncertainties. Method A, the gravimetric method, is overall less sensitive to operator error and lacks steps that are delicate. Using both methods side by side was motivated by a wish to verify gelatines anisotropic abilities.

Another source of uncertainties is that the gel starts to fall apart around the edges, with handling and long periods of swelling, this is particular true of Method A. Why this might be is discussed more under Swelling below. For the gel in general, it is assumed that the swelling is unidirectional due to the gelatine's anisotropic property. However, it is questionable whether the swelling is one directional in small pieces that has detached from the gel. Depending on the properties of the surface that connected the rest of the gel with the detached piece, could the swelling be two-directional for the detached piece which is floating freely in the solvent.

Method B

Due to the inability to generate any consistent results, will the rest of the discussion be based on primarily the data from method A, the gravimetric method.

Swelling

Note that the different swelling curves made of different amounts of gelatinous liquid are not side by side comparable, due to the fact that the time axis is not normalised. The total amount of time the gels swells is a function of the initial thickness. The time it takes for a gel to swell to its maximum capacity can at best be estimated, but mostly it cannot since the gels break down via leaching after a couple of days in water and it seems that a gel does not reach the volume (for instance 5.00 ml) at which it was made. The total amount of solvent the gel is willing to absorb is dependent on the temperature of the solvent.

Different states of swelling

First of all to clearly notice the different states through which the gel swells in (amorphous, intermediate and crystalline) is a first. It is not observed due to a novel measuring system, but with more thorough analysis of the data. So far have they only been mentioned in a theoretical sense, without any use of measured data to back them up.

One notices in figure 15 that the lines describing the different phases are not quite straight, this is extra apparent on the intermediate trends curves. Moreover, they tend to bulge on the middle which indicate a systematic error, hence the data ought to be a curve of higher degree. However, it is likely that the gel is not entirely in the same phase, meaning that top and bottom is not always the same. It is also possible that the transition regions are notable longer than assumed.

When the matrix reach $\varphi_w=0.88$ it change from the amorphous to intermediate phase, regardless of initial gel thickness. This is also a first time observation that the change is that well-defined and precise. Exactly at what volume fraction this will happen is most likely dependent on the gelatine's manufacturing method, the concentration of gelatine in the casting solution and other factors, it maybe even be solvent dependent. If one would do simulations of the gel it would be desirable to take into account that the gel will change its physical properties around this volume fraction.

Given the rheological results (see figure 20 and 21) on the gels that has swollen in 21 °C for 12 and 13 hours, according to the phase angle acquired with the frequency sweep, they are clearly in the regime (~10^{-2}) of being glassy crystalline polymers (STEFFE, 1996), which fits very well with the analysis done with the time dependent model. Otherwise is the comparison between a freshly made and a rehydrated/swollen gel about the same. However, the fresh and rehydrated samples were from different batches and made of different amounts of gelatine liquid (fresh: 5.00 ml, rehydrated: 4.2 ml).

Temperature and glass transition

Since the swelling velocity and the swelling capacity are dependent on temperature, one may conclude that the matrix relaxation is aided by a higher temperature. As will be further developed under Models is the structural tension in the gel matrix substantial and appears to be one of the major factors in controlling the swelling. It makes sense that the extra energy in form of a higher environment temperature helps the matrix to undo its internal tension quicker than what would otherwise be possible. The transport modes (see eq. 1, table 1 and figure 15) are linear in the given temperature range, indicates that the matrix is highly ordered.

A rather surprising discovery is that the intermediate state only exists below the glass transition temperature, and above it the gel stop to swell and starts to melt away. It is also rather peculiar to find that the predicted transport mode around the glass transition point for once follow the ideal Fick's law. That the gel melts away clearly suggests that the physical properties of the gel change (most notably the melting point change) when going from the amorphous phase into the intermediate phase.

That the swelling capacity seems to be increasing with temperature and even surpass the initial casting volume for some samples at 25.5 and 27.5 °C, might because that the gel matrix is more susceptible to heat damage and therefore undergo a structural change that will alter the swelling capacity of the gel. It is however observed by Shreve (SHREVE, 1919) that the swelling equilibrium is temperature dependent, and if the temperature is further increased after the equilibrium has been obtained, it will continue to swell. Also, if the temperature is lowered after the equilibrium has been reached; the gel will not lose any of the solvent it has absorbed.

Transitional regions

The observed transitions between different phases can be explained with that the top layer of the gel has already reached into the next phase, while a sizeable part of the gel further away from the diffusion surface is still in the current phase. If so, the size of the transition regions would then depend on the gel internal diffusion. One does notice that they are harder to detect in films made from less gelatine solution (i.e. 1.8 ml) compared to thicker films (i.e. 7.2 ml). If one assumes that the top layer moves down through the gel at a fairly fix speed regardless of thickness, then there will automatically be fewer data points of the transitional regions in a thin gel than in a thick gel.

Intermediate region

The exact nature of the intermediate region is unclear. It might be the metastable result of the amorphous gel trying to reach the crystalline state. It might be a mesomorphic region, as have been speculated (Shepard, 1923), but given what we know about liquid crystal displays (LCD) and similar applications does gelatine seem remote in its properties to qualify into being an even partial mesomorphic material. This distinct region might be another version of the amorphous state but where the predominate active force would have changed. However, one would not expect such a clear break into this new region, but a much more gradual transition, if it was still the same.

If one considers the profile of the drying process (see figure 24), it does appear that the drying only goes through two states or regions, which would imply that the intermediate swelling region is just a transitional state. However, it might be that there is a different mechanism when drying the gels to films and when they rehydrate and swell from films to gels.

Region IV, or odd swelling behaviour?

Although a bit of a mystery, a forth region is observable in 5.00 ml and 1.8 ml gels (see figure 16 and table 3) when they are allowed to swell for a considerable amount of time. Do note that this region is only observed at 21 °C, and the gels have stopped swelling completely at higher degrees. So it is possible that this region only exists at lower temperatures. It cannot be disregarded that it is a second stage of the crystalline region or that it is the actual crystalline state, hence that the “crystalline region” would a mere transitional region.

The fourth region could be due to the same effect as the transitional regions, that the top bits of the gel has finished to swell, while those part of the gel that are not in direct contact with the swelling surface, would have to depend on the gels internal diffusion, hence the swelling speed would seem anomalous, which might explain the in some gels observed fourth region of swelling.

Another possibility could be that the gel has started to dissolve or leach as noted with the 5.00 ml gels, since the weak intermolecular forces between the alpha-helices has weaken due to the increased gel volume, or that it has finally become thermodynamically more beneficial to break loose from the gel matrix. That it does take at least 100 hours at room temperature before it happens is probably due to the large molecular size of the polymer strands, $2.0 \cdot 10^4 - 2.4 \cdot 10^5$ Da, hence making free and unhindered diffusion into the solvent rather unlikely and time consuming. However, this phenomenon is also observed in the relatively thin 1.8ml gel, so this cannot be the only explanation.

An explanation that would also seem likely for even the 1.8ml gels, is that the alpha-helices have start to loosen up after a considered amount of swelling in the crystalline state. The helices would loosen up due to the internal tension within each fibre-strand, because of the all solvent stretching the gel matrix. The loosening inside the helices would result in that the gel volume would allow for more swelling than otherwise would be possible at the given temperature, but ultimately result in the gel to decay.

Ofner’s (Ofner, 1986) observation on this matter is that leaching is highly dependent on storage environment and how old the film was when swollen. For instance a 39 month old gel, stored at room temperature, lost a quarter of its matrix after 96 hours of swelling. The level of humidity and storage temperature are key factors. An increased leaching is ascribed to a slight hydrolytic degradation during swelling.

Models

There are a couple of models that have been used for gelatine swelling and they deserve a thorough comment and analysis, since at least the Hofmeister, Robinson and Ofner models share a great deal of similarities and can be argued, as will be shown, that they are the same quasi-second-order model. Ultimately also why they are insufficient models when compared to the pseudo-sigmoid model. All the models. It is rather revealing that roughly the same model has been independently discovered at least three times in the history of the study of gelatine's swelling (i.e. 1890, 1964, 2009).

The time-dependent model has generated some rather revealing results and has for the first time given support from data for the existence of the different phases that gelatine undergoes during swelling. However, it is the most complicated to use for that purposes of prediction since it will require more calculations to predict the different constants, such as Arrhenius coefficients and transport mode, for the different parts of the swelling curve. On the other hand, we no longer live in the 19th or 20th century and computer power is cheap.

Comparison between the pseudo-second order models

The Hofmeister model

Hofmeister insists to insert $P - W = \dfrac{P}{1+\frac{c}{d}t}$ into the models derivate, which one then acquires

$$\frac{dW}{dt} = (P - W)\frac{\frac{c}{d}}{1+\frac{c}{d}t} \text{ (HOFMEISTER, 1890) or written as } \frac{dW}{dt} = f(t)(P - W).$$

This resembles Robinson's assumed derivate $\frac{dW}{dt} = k(W_\infty - W)^2$, especially since $P = W_\infty$, but where k is no longer a constant but a function *f(t)* to compensate for the lack of the square found in Robinson's model. Apparently, the given *f(t)* is an acceptable approximation in solvents with high salt concentrations, but as the salinity drops to normal or non-existent levels, Hofmeister's model shows its inherent design flaw, as have been demonstrated (SHEPARD ,1923).

The Robinson and Ofner models

For the derivate given by Robinson with the given the boundary value $W(0) = 0$ will produce

$$W = \frac{kW_\infty^2 t}{1 + kW_\infty t} \text{ (ROBINSON, 1964) or } W = \frac{kW_\infty^2}{1/t + kW_\infty} = \frac{1}{kW_\infty^2/t + W_\infty^{-1}} \text{ given } t \neq 0.$$

The latter expression of the Robinson model resembles very much a derivation of the Ofner model:

$$\frac{t}{W} = A + Bt \text{ or } W = \frac{1}{A/t + B} \text{ given } t \neq 0.$$

The expressions are equal if

$$\begin{cases} A = kW_\infty^2 \\ B = W_\infty^{-1} \end{cases}$$

Please note that A is, as stated earlier according to Ofner (OFNER, 1986), a linear function of the initial thickness (H) of the non-swollen gel, hence $kW_\infty^2 = \alpha H + \beta$ given the correlation above, where $\beta \approx 0$. Please note that the left hand side is a homogenous model and the right hand side is a linear model. They can only be approximately each at small values and where $\beta \approx 0$. All the variables are solvent and/or gel specific.

The modified Hofmeister model

If one indulge in giving Hofmeister a second chance, and if one ignores Hofmeister's own dubious substitution with $P - W$ and instead substitute with $C = c/d$, another more familiar formula will occur.

$$W = P\left(1 - \frac{1}{1+Ct}\right) = P - \frac{P}{1+Ct} = \frac{P(1+Ct) - P}{1+Ct} = \frac{CPt}{1+Ct} \overset{t \neq 0}{=} \frac{CP}{1/t + C} = \frac{1}{CP/t + P^{-1}}$$

As previously known is $P = W_\infty$, and assume $C = kW_\infty$, hence giving

$$W = \frac{1}{kW_\infty^2/t + W_\infty^{-1}}$$, i.e. the Robinson model, which is equal to the Ofner model.

Furthermore c is a gel-solvent specific constant and d is the initial thickness of the gel, thus making it possible to substitute c/d with a more general gel-solvent specific constant such as C.

All the three different models are in essence the same pseudo-second order model. Hofmeister just defined his constants wrong. Shepard's (SHEPARD, 1923) dismissal of the Hofmeister model, seems in retrospect to have been premature.

Time-dependent model for polymers in general

The transport mode (n) varies all over the spectrum depending on swelling state. The rapid transport mode between 0.5 and 0.7 (see table 4) in the initial amorphous swelling, as observed in this temperature interval, is likely to be due to the structural tension within the matrix that makes it thermodynamically more beneficial for a rapid expansion of the matrix as soon as the matrix gains access to water. In later stages the transport mode is slower than Fick's law ($n=½$), can be interpret as that structural tension is considerably lower, and that the matrix' own weight becomes a limiting factor on the speed it may swell. Gelatine is after all made up by macro molecules with a molecular weight of $2.0 \cdot 10^4$ – $2.4 \cdot 10^5$ Da.

It is also reasonable to assume that the osmotic pressure, as a driving force becomes a less relevant factor for swelling, the more solvent that has been absorbed by the matrix.

The Pseudo-Sigmoid Model (PSM)

The usage of the PSM (see eq. 18 & 20) is founded in the observation that the data points form a distinct S-shape (see figure 17) when the time-axis has been logarithmised. The PSM describes the accumulation of solvent inside the gel over time. The model has only been verified with gravimetric data.

$$W = \frac{A}{1 + Be^{-Cx}} \overset{x=\ln t}{=} \frac{A}{1 + Be^{-C\ln t}}$$ which gives the following when simplified

$$W = \frac{A}{1 + B/t^{C}} \qquad \text{(Eq. 18)}$$

$$\frac{dW}{dt} = \frac{ABCt^{-C-1}}{\left(1 + B/t^{C}\right)^{2}} \qquad \text{(Eq. 20)}$$

Validity of the PSM

The model's derivate, dW/dt, compare well with the estimated swelling velocity (see figure 25). There is fairly randomised distribution of the points. Note that the $\Delta W/\Delta t$ values are in a sense estimated since they are calculated from the measured W and t. Because of this does $\Delta W/\Delta t$ have uncertainties in both axes.

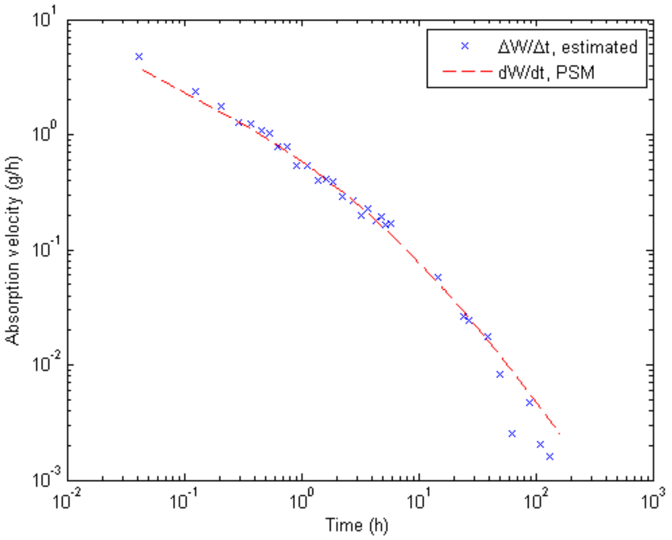

Figure 25. Plot showing a match between the estimated absorption velocity and the PSM's absorption velocity for a film made out of 5ml solution, swollen at 21 °C for 168 hours.

PSM compared to the Ofner model

As seen in figure 26, is the Ofner model (see eq. 6) build around the premise that t/W would fit a straight line, as would be the case if the swelling process was a second-order reaction. Ofner (OFNER, 1986) claim the curve fit to be satisfactory, despite the distribution of data points being far from randomly distributed above and below the line. However, the data points are distributed so that the points near the middle of the line are above and below near the ends. This implies that the data cannot be approximated with a straight line, although the data points are neatly lined up. As shown above is the Ofner, Robinson and Hofmeister model the same model, so this criticism ought to apply to all of them. As seen in figure 26, does the PSM not have this problem.

It has been (ROBINSON, 1964) shown however, that it might be an acceptable approximation for very thin gelatine film layers, where the different phases of gelatine does not distinguish themselves as much. As discussed under the Swelling section, are these regions and their characteristics

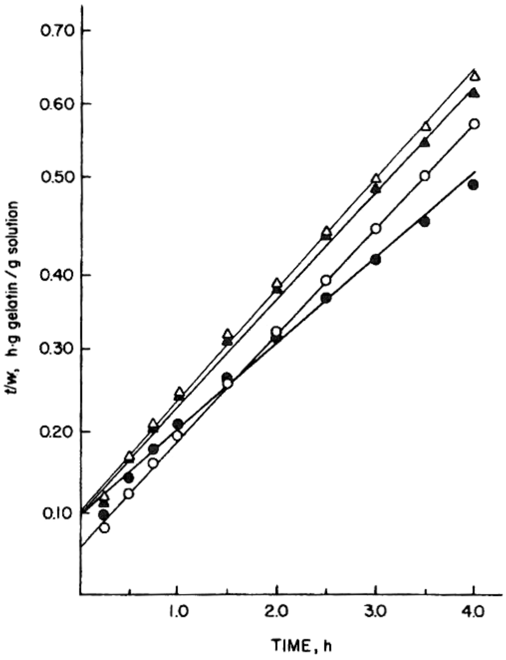

Figure 26. Showing swelling data and how it fits the Ofner model. (OFNER, 1986)

easier to observe with gels of greater initial thickness.

The Ofner model use the ratio between solvent imbibed and the initial mass of the gel network (W) instead of just the imbibed solvent into the gel. This has no effect on the comparison, since the mass of the gel network is constant.

Ofner (Ofner, 1986) recommends that one makes two curve fits, one for predicting swelling for the first few hours (0 – 4 hours) and one for longer periods (using the entire data set). This effectively gives the model not two variables, but four. The PSM has three.

Drying film

The drying was performed with a slight elevation with an angle of approx. 30° so most of the air flow from the air conditioner could be used. There are no indications that the drying would have been uneven due to this. Mainly because the drying seems to be limited by what is thermodynamically possible, and the calculated water level in these films and those dried on a flat surface were identical.

Storage of film

When storing films in cold temperature, according to protocol, the results from experiments imply that the gels can be stored for at least 4-6 week without any noticeable effects on swelling performance. It has also been shown by others (Shreve, 1919; Ofner, 1986) that aging is not an issue for the readiness to swell. Ofner (Ofner, 1986) makes the observation that substantially older films have a greater tendency to leach when swollen for an extended period of time, i.e. a couple of days. In this context ought 4-6 week old films considered to be fresh films.

Gelatine gel density

It is important to differentiate between the density of a freshly set gel and a swollen gel, since the density of the gel is a function of the water content. The gel density of a swelling gel will be changing the most during approximately the first hour of swelling, since after that the water content (φ_w) will be above 0.9.

Volume fraction of solvent

The volume fraction of solvent is defined as

$$\varphi_w = \frac{V_{solvent}}{V_{total}}, \text{ where } V_{total} = V_{solvent} + V_{matrix,amorphous} \text{ and } V_{matrix,amorphous} = m_{initial,dry} / \rho_{film,amorphous} .$$

It is difficult to confirm whether if the assumption that the total volume of the gel is the sum of the volume of the solvent and the volume of the amorphous gelatine matrix, is good one or not. Nonetheless, it is important to have at least a fair estimate of volume fraction so the swelling process may be tracked and compared.

The core problem is whether the solvent and the matrix has any substantial molecular interaction or not. However, because gelatine has about equal amounts of polar and non-polar regions on its strands it is possible that both the attraction and repulsion of solvent will cancel each other out. Also, that both these forces probably has a rather negligible effect on the measurement.

Dry gelatine film density

Although it is expected for the gelatine film to have a slightly lower density than the gelatine sheet from which it was made, since 100% efficiency cannot be expected. It is however not all obvious if the difference is actual or not. The issue of comparing the density of the gelatine sheets and the density of the dried gelatine film density is of a methodological character. The gelatine sheets were homogenous in their thickness, hence a standard deviation could easily been estimated since the sheet should be assumed to be a rather flat slab.

With the gelatine film however, it was decided to be most accurate to use a film that had detached voluntarily due to its extreme thinness (a couple of micrometres). As previously mentioned, the film was characterised as fragile and brittle. Gelatine films with similar physical characteristics had <2% water content (OFNER, 1986), so it seems reasonable to assume that the self-detached film had an exceptionally low water content. Therefore it seemed unlike that the remaining water content would have an effect on the overall measurements, hence was neglected. The decision of using a self-detached film was partially based on the risk of further compress or damage the film if it was extracted by force from the discs it was let to dry, hence generate incorrect results.

Even if the self-detached film was also approximated to be a cuboid, its actual shape was more of a ski slope. Hence, the different thicknesses that was measured over the surface gives the film a rather large standard deviation for the thickness as a whole. In retrospect it seems that more care should have been taken to ensure to develop a method of extracting dried film that is more suitable for a direct comparison.

However, if one does assume that the ski-slope sample has the same 95% interval as the Marks & Spencer sample, which is the much more narrow of the two, one receives the following:

$$\mu_{M\&S} = 1290.9 \pm 10.5\, kg/m^3$$

$$\mu_{ski} = 1274.0 \pm 10.5\, kg/m^3$$

Hence, the null hypothesis *H₀:* $\mu_{M\&S} = \mu_{ski}$ would be trivially true, and there would be no significant difference between them.

CONCLUSIONS

- What are the properties of the gel during swelling and do they change?

Properties change according to which state the gel is in.

- How does temperature affect the swelling trends?

Above the glass temperature, the gelatine gel will not swell beyond the amorphic state.

- With which states can the swelling profile of gelatine be described?

The swelling states are Amorphic, Intermediate and Crystalline.

- Can a more precise model be found to describe the swelling of gelatine?

Yes, the PSM is better than the Robinson-Ofner model. The Time Dependent model is even more precise but impractical.

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ABBREVIATIONS

a	for the Robinson model: a gel and solvent specific constants
A	for the Ofner model: a gel specific constant which is linearly dependent on the initial thickness of the gel
b	for the Robinson model: a gel and solvent specific constants
B	for the Ofner model: the inverse of W_∞
c	for the Hofmeister model: a gel and solvent specific constant
d	for the Hofmeister model: the average thickness of gel when swollen to its' maximum
H	for the Ofner model: the initial thickness of the non-swollen gel
k	for the time-dependent model: the adsorption speed for the Robinson model: a gel and solvent specific constant.
n	for the time-dependent model: the transport mode
NTP	Normal Temperature Pressure, 21 °C, 1 atm
P	for the Hofmeister model: the maximum amount of solvent that the gel can absorb
t	for all models: time
T	temperature
V	volume
W	for all models: mass of imbibed solvent
W_∞	for the Robinson model: the mass of imbibed water at equilibrium for the Ofner model: the maximum uptake as shown in experiments
φ_w	Water content in gel.

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Private communications

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APPENDIX

I: Procedure for film making

1. Soak 5.95 g of Marks & Spencer gelatine leafs (84 % protein, batch 9026) in 100 ml of room temperate reverse osmosis water. Soak them for at least 10 minutes, as recommended on the package.

2. Heat the water with the leafs while steering on low heat (<50 °C). When it has melted completely and no protein strands can be visually observed in the liquid, add a drop of food colouring (E124).

3. Add 5 ml of gelatine liquid on top of a stainless steel disc with a diameter of 50 mm in a petri dish. The stainless steel discs must have been scrubbed thoroughly and then soaked in acetone for a minimum of 1½ hours. If the discs have not been scrubbed thoroughly enough they will be covered with a film after the acetone-bath. Apply the liquid on stainless steel plates that have been taken directly from the acetone-bath, after the acetone has evaporated. Do not touch the edges or the top, touch the underneath of the disc when moving it.

4. Let the films set at cold temperature (about 3 °C) for 5 minutes or at room temperature for 30 minutes. When producing thicker films (about 5 ml or more of gelatine solution) should let to be set in room temperature, since the surface easily can be disturbed and the liquid gelatine run off the discs.

5. Let the films dry in front of an air conditioner, so the drying velocity surpasses 0.24 g solvent/hour, hence avoid the formation of air bubbles inside the dry gel. After 24 hours has the drying process stopped, and will not lose any more solvent.

6. Store the films in the cold room for future use. Please see chapter on discussion of drying films.

II: Coefficients for models

Kinetics model

Coefficients (see table 5) from regression for the kinetics model

$$W = \frac{A}{1 + B/t^{C}} \qquad \text{(Eq. 18)}$$

Table 5. Coefficients for model for 21.0 °C given different casting volumes of gel, acquired via least square method.

	A	B	C
1.8 ml	0.926454	0.396088	0.807595
4.2 ml	2.47594	0.838954	0.810112
5.00 ml	5.64835	3.02674	0.55763
7.2 ml	6.88306	3.56688	0.53888

III: Calculations

The Robinson model

Robinson estimates that the swelling is best described as a quasi-second-order reaction

$$\frac{dW}{dt} = k\left(W_{\infty} - W\right)^2 \quad \text{(Eq. 5)}$$

If one separate and integrate the above expression this follows

$$\int \frac{dW}{\left(W_{\infty} - W\right)^2} = \int k dt$$

$$\frac{1}{W_{\infty} - W} = kt + C$$

Given that the nothing has swollen at point zero one acquires the following

$$W(0) = 0 \Rightarrow \frac{1}{W_{\infty}} = C$$

Put in the expression above gives

$$\frac{1}{W_{\infty} - W} = kt + \frac{1}{W_{\infty}}$$

$$0 = kW_{\infty}^2 t - W\left(1 + kW_{\infty} t\right)$$

Hence, the Robinson model.

$$W = \frac{kW_{\infty}^2 t}{1 + kW_{\infty} t} \qquad \text{(Eq. 21)}$$

VI: Data series

Rheology

Amplitude sweep

Fresh gel

Time *s*	Temp. *°C*	Freq. *Hz*	Complex Modulus *Pa*	Elastic Modulus *Pa*	Viscous Modulus *Pa*	Complex Viscosity *Pas*	Phase Angle *°*	Shear Stress *Pa*	Strain	Acc. Time *s*	Ang. Freq. *rad/s*	Torque *Nm*	Eta Double Prime *Pas*	Dyn. Vis. *Pas*
50.85	21	1	500.4	495.1	72.65	79.64	8.348	0.02444	5.137E-5	50.85	6.283	9.998E-8	78.8	11.56
100.7	21.1	1	571.3	566.2	76.81	90.93	7.726	0.02918	5.338E-5	100.7	6.283	1.194E-7	90.11	12.22
151	21	1	553.2	549.3	65.2	88.04	6.768	0.03485	6.594E-5	151	6.283	1.425E-7	87.43	10.38
200.9	20.9	1	590	589.6	21.84	93.9	2.122	0.04161	7.364E-5	200.9	6.283	1.702E-7	93.84	3.476
251.4	21	1	565.2	562.2	57.98	89.96	5.888	0.04968	9.192E-5	251.4	6.283	2.032E-7	89.48	9.227
302.7	21	1	594.6	594	26.71	94.64	2.575	0.0593	0.0001041	302.7	6.283	2.426E-7	94.54	4.252
353.8	21	1	546.4	545.4	32.54	86.95	3.414	0.07078	0.0001357	353.8	6.283	2.895E-7	86.8	5.178
404.1	21	1	583.4	582.5	33.33	92.85	3.275	0.08451	0.0001513	404.1	6.283	3.457E-7	92.7	5.304
454.2	21	1	577.8	576.5	38.89	91.96	3.859	0.1009	0.0001825	454.2	6.283	4.129E-7	91.75	6.19
504.1	20.9	1	585.9	585.5	21.13	93.24	2.066	0.1205	0.0002148	504.1	6.283	4.928E-7	93.18	3.362
553.9	21	1	592.3	592.1	14.88	94.27	1.44	0.1439	0.0002536	553.9	6.283	5.886E-7	94.24	2.368
604	20.9	1	598.4	597.6	30.91	95.25	2.961	0.1718	0.0002995	604	6.283	7.026E-7	95.12	4.92
654.2	20.9	1	603.6	602.9	27.89	96.06	2.648	0.2051	0.0003544	654.2	6.283	8.389E-7	95.96	4.439
704.7	21	1	610.3	609.9	22.85	97.13	2.146	0.2447	0.0004181	704.7	6.283	1.001E-6	97.07	3.637
755.5	20.9	1	617.3	616.9	22.94	98.25	2.129	0.2923	0.0004934	755.5	6.283	1.196E-6	98.18	3.65
806.5	21.1	1	618.1	617.6	24.22	98.37	2.246	0.349	0.0005884	806.5	6.283	1.428E-6	98.3	3.855
857.9	21	1	625.3	625	20.17	99.52	1.848	0.4167	0.0006941	857.9	6.283	1.705E-6	99.47	3.21
907.9	21	1	628.1	627.8	19.51	99.96	1.78	0.4974	0.0008248	907.9	6.283	2.035E-6	99.91	3.106
957.8	21	1	629.9	629.8	15.25	100.3	1.387	0.5939	0.0009817	957.8	6.283	2.43E-6	100.2	2.428
1008	21	1	634.1	633.8	19.23	100.9	1.738	0.709	0.001164	1008	6.283	2.9E-6	100.9	3.061
1058	21	1	635.6	635.4	16.82	101.2	1.516	0.8465	0.001386	1058	6.283	3.463E-6	101.1	2.676
1109	21	1	638.4	638.1	18.13	101.6	1.627	1.01	0.001647	1109	6.283	4.133E-6	101.6	2.885
1159	21	1	644.2	644	16.34	102.5	1.453	1.206	0.001948	1159	6.283	4.935E-6	102.5	2.6
1211	21	1	649	648.8	17.65	103.3	1.558	1.441	0.002308	1211	6.283	5.893E-6	103.3	2.808
1262	21.1	1	649.7	649.5	16.28	103.4	1.436	1.72	0.002752	1262	6.283	7.034E-6	103.4	2.591
1313	21	1	655.2	655	16.38	104.3	1.433	2.053	0.003257	1313	6.283	8.397E-6	104.2	2.607
1364	21	1	658.8	658.6	16.14	104.9	1.404	2.452	0.003868	1364	6.283	1.003E-5	104.8	2.568
1414	21	1	663.4	663.2	15.82	105.6	1.366	2.927	0.004585	1414	6.283	1.197E-5	105.6	2.518
1465	21	1	666.5	666.3	15.9	106.1	1.367	3.495	0.005447	1465	6.283	1.43E-5	106.1	2.531
1516	21	1	668.5	668.3	16.35	106.4	1.402	4.171	0.006481	1516	6.283	1.706E-5	106.4	2.603
1566	20.9	1	671.5	671.3	15.86	106.9	1.353	4.98	0.007702	1566	6.283	2.037E-5	106.8	2.524
1616	21	1	674.4	674.2	15.78	107.3	1.341	5.945	0.009155	1616	6.283	2.432E-5	107.3	2.512
1667	21	1	678.2	678	15.99	107.9	1.351	7.1	0.01087	1667	6.283	2.904E-5	107.9	2.544
1716	21.1	1	680.5	680.3	15.67	108.3	1.32	8.474	0.01293	1716	6.283	3.466E-5	108.3	2.494
1767	21	1	683.4	683.2	16.11	108.8	1.351	10.12	0.01537	1767	6.283	4.14E-5	108.7	2.564

1819	21	1	685.8	685.6	16.07	109.1	1.343	12.08	0.01828	1819	6.283	4.941E-5	109.1	2.557
1869	21.1	1	687.6	687.4	15.8	109.4	1.316	14.42	0.02177	1869	6.283	5.901E-5	109.4	2.514
1920	21	1	688.8	688.6	15.74	109.6	1.309	17.22	0.02594	1920	6.283	7.044E-5	109.6	2.505
1970	21	1	690.3	690.1	15.76	109.9	1.308	20.56	0.0309	1970	6.283	8.411E-5	109.8	2.508
2020	21	1	690.7	690.5	15.77	109.9	1.309	24.54	0.03686	2020	6.283	0.0001004	109.9	2.51
2070	20.9	1	691	690.8	15.93	110	1.321	29.3	0.04399	2070	6.283	0.0001199	109.9	2.535
2121	20.9	1	692	691.8	15.97	110.1	1.322	34.99	0.05245	2121	6.283	0.0001431	110.1	2.541
2171	21	1	694	693.8	15.62	110.5	1.289	41.77	0.06243	2171	6.283	0.0001709	110.4	2.485
2221	21	1	697.5	697.3	15.61	111	1.282	49.86	0.07414	2221	6.283	0.000204	111	2.485
2272	21	1	704	703.9	16.06	112.1	1.307	59.52	0.08764	2272	6.283	0.0002435	112	2.556
2322	21.1	1	713.6	713.4	16.33	113.6	1.311	71.11	0.1033	2322	6.283	0.0002909	113.5	2.599
2372	21.1	1	719.3	719.1	15.66	114.5	1.248	84.81	0.1221	2372	6.283	0.0003469	114.5	2.492
2423	21.1	1	724.2	724	16.66	115.3	1.318	101.3	0.1449	2423	6.283	0.0004144	115.2	2.652
2473	21.1	1	727.2	727.1	16.02	115.7	1.262	121	0.1722	2473	6.283	0.0004948	115.7	2.549
2523	21.1	1	732.2	732.1	16.12	116.5	1.261	144.4	0.2042	2523	6.283	0.0005909	116.5	2.565
2573	21	1	736.2	736	16.33	117.2	1.271	172.5	0.2425	2573	6.283	0.0007055	117.1	2.598
2623	21	1	743.5	743.3	16.66	118.3	1.284	205.9	0.2865	2623	6.283	0.0008422	118.3	2.652
2673	21	1	752.3	752.2	16.83	119.7	1.282	245.8	0.3379	2673	6.283	0.001005	119.7	2.679
2723	21	1	760.8	760.6	16.88	121.1	1.272	293.4	0.3987	2723	6.283	0.0012	121.1	2.687
2773	21.1	1	771.9	771.7	17.37	122.9	1.29	350.4	0.469	2773	6.283	0.001433	122.8	2.765
2823	21	1	785.2	785	18.35	125	1.339	418.2	0.55	2823	6.283	0.001711	124.9	2.921
2873	20.9	1	798.4	798.2	20.87	127.1	1.498	499.4	0.6457	2873	6.283	0.002043	127	3.322
2923	21	1	812.8	812.4	26.59	129.4	1.875	596.2	0.7567	2923	6.283	0.002439	129.3	4.233
2973	21	1	827.8	827	35.03	131.7	2.425	711.9	0.8867	2973	6.283	0.002912	131.6	5.575
3023	21	1	838.2	836.8	49.22	133.4	3.367	849.6	1.045	3023	6.283	0.003475	133.2	7.834
3073	20.9	1	809.9	805.9	80.39	128.9	5.697	1014	1.292	3073	6.283	0.004149	128.3	12.8
3123	21	1	17.3	1.516	17.23	2.753	84.97	1211	41.66	3123	6.283	0.004955	0.2413	2.743
3173	21	1	12.26	1.242	12.2	1.951	84.18	1446	54.24	3173	6.283	0.005913	0.1977	1.941
3222	21	1	11.88	3.177	11.45	1.89	74.49	1727	56.88	3222	6.283	0.007063	0.5056	1.822
3272	20.9	1	18.64	12.55	13.78	2.967	47.66	2061	51.59	3272	6.283	0.00843	1.998	2.193
3322	21	1	29.89	25.29	15.92	4.757	32.19	2461	46.71	3322	6.283	0.01007	4.026	2.534
3372	20.9	1	43.01	39.13	17.86	6.845	24.53	2938	44.17	3372	6.283	0.01202	6.228	2.842
3422	20.9	1	55.81	52.72	18.31	8.882	19.16	3507	43.96	3422	6.283	0.01435	8.39	2.915
3472	21	1	68.55	66.02	18.46	10.91	15.62	4187	45.12	3472	6.283	0.01713	10.51	2.938
3522	21	1	84.21	82.06	18.91	13.4	12.98	5001	46.03	3522	6.283	0.02046	13.06	3.01

Rehydrated gel

Time *s*	Temp. *°C*	Freq. *Hz*	Complex Modulus *Pa*	Elastic Modulus *Pa*	Viscous Modulus *Pa*	Complex Viscosity *Pas*	Phase Angle *°*	Shear Stress *Pa*	Strain	Acc. Time *s*	Ang. Freq. *rad/s*	Torque *Nm*	Eta Double Prime *Pas*	Dyn. Vis. *Pas*
50,27	21	1,00E+00	0,5	1,41E+03	1,41E+03	1,22E+01	2,24E+02	2,45E-02	1,74E-05	50,27	21	1,00E+00	0,5	1,41E+03
100,177	21	1,00E+00	12	1,37E+03	1,34E+03	2,85E+02	2,18E+02	2,92E-02	2,14E-05	100,177	21	1,00E+00	12	1,37E+03
150,825	21	1,00E+00	7,9	1,28E+03	1,26E+03	1,75E+02	2,03E+02	3,49E-02	2,75E-05	150,825	21	1,00E+00	7,9	1,28E+03
200,471	21	1,00E+00	5,7	1,21E+03	1,21E+03	1,20E+02	1,93E+02	4,16E-02	3,45E-05	200,471	21	1,00E+00	5,7	1,21E+03
252,043	21	1,00E+00	5,1	1,33E+03	1,32E+03	1,17E+02	2,12E+02	4,97E-02	3,76E-05	252,043	21	1,00E+00	5,1	1,33E+03

302,673	21	1,00E+00	7,6	1,26E+03	1,25E+03	1,67E+02	2,01E+02	5,93E-02	4,74E-05	302,673	21	1,00E+00	7,6	1,26E+03
352,172	20,9	1,00E+00	2	1,26E+03	1,26E+03	4,49E+01	2,01E+02	7,08E-02	5,65E-05	352,172	20,9	1,00E+00	2	1,26E+03
404,569	21	1,00E+00	2,1	1,27E+03	1,27E+03	4,70E+01	2,01E+02	8,45E-02	6,72E-05	404,569	21	1,00E+00	2,1	1,27E+03
454,762	21	1,00E+00	4,5	1,26E+03	1,25E+03	9,79E+01	2,00E+02	1,01E-01	8,08E-05	454,762	21	1,00E+00	4,5	1,26E+03
505,302	21	1,00E+00	3,3	1,32E+03	1,32E+03	7,63E+01	2,11E+02	1,20E-01	9,16E-05	505,302	21	1,00E+00	3,3	1,32E+03
556,286	21	1,00E+00	2,9	1,27E+03	1,27E+03	6,49E+01	2,03E+02	1,44E-01	1,14E-04	556,286	21	1,00E+00	2,9	1,27E+03
607,578	21	1,00E+00	2,5	1,29E+03	1,29E+03	5,62E+01	2,06E+02	1,72E-01	1,34E-04	607,578	21	1,00E+00	2,5	1,29E+03
657,933	21,1	1,00E+00	1,7	1,30E+03	1,30E+03	3,95E+01	2,07E+02	2,05E-01	1,59E-04	657,933	21,1	1,00E+00	1,7	1,30E+03
708,962	21,1	1,00E+00	1,9	1,32E+03	1,32E+03	4,28E+01	2,10E+02	2,45E-01	1,87E-04	708,962	21,1	1,00E+00	1,9	1,32E+03
760,225	21	1,00E+00	2	1,31E+03	1,31E+03	4,57E+01	2,08E+02	2,92E-01	2,25E-04	760,225	21	1,00E+00	2	1,31E+03
811,157	21	1,00E+00	2,1	1,33E+03	1,33E+03	4,86E+01	2,11E+02	3,49E-01	2,64E-04	811,157	21	1,00E+00	2,1	1,33E+03
862,248	21	1,00E+00	2	1,31E+03	1,31E+03	4,61E+01	2,09E+02	4,17E-01	3,19E-04	862,248	21	1,00E+00	2	1,31E+03
913,247	21,1	1,00E+00	1,3	1,30E+03	1,29E+03	3,05E+01	2,06E+02	4,97E-01	3,87E-04	913,247	21,1	1,00E+00	1,3	1,30E+03
964,139	21	1,00E+00	1,6	1,30E+03	1,30E+03	3,59E+01	2,06E+02	5,94E-01	4,61E-04	964,139	21	1,00E+00	1,6	1,30E+03
1015,454	21	1,00E+00	1	1,30E+03	1,30E+03	2,37E+01	2,07E+02	7,09E-01	5,47E-04	1015,454	21	1,00E+00	1	1,30E+03
1065,717	21	1,00E+00	1,6	1,30E+03	1,30E+03	3,53E+01	2,07E+02	8,46E-01	6,56E-04	1065,717	21	1,00E+00	1,6	1,30E+03
1116,175	20,9	1,00E+00	1,5	1,31E+03	1,31E+03	3,47E+01	2,08E+02	1,01E+00	7,78E-04	1116,175	20,9	1,00E+00	1,5	1,31E+03
1167,385	21	1,00E+00	1,3	1,30E+03	1,30E+03	2,85E+01	2,07E+02	1,21E+00	9,33E-04	1167,385	21	1,00E+00	1,3	1,30E+03
1217,73	21	1,00E+00	1,3	1,31E+03	1,30E+03	2,94E+01	2,08E+02	1,44E+00	1,11E-03	1217,73	21	1,00E+00	1,3	1,31E+03
1268,389	20,9	1,00E+00	1,3	1,30E+03	1,30E+03	2,99E+01	2,07E+02	1,72E+00	1,33E-03	1268,389	20,9	1,00E+00	1,3	1,30E+03
1318,686	21	1,00E+00	1,3	1,31E+03	1,31E+03	3,04E+01	2,08E+02	2,05E+00	1,58E-03	1318,686	21	1,00E+00	1,3	1,31E+03
1368,833	21	1,00E+00	1,3	1,31E+03	1,31E+03	3,05E+01	2,08E+02	2,45E+00	1,89E-03	1368,833	21	1,00E+00	1,3	1,31E+03
1419,614	21	1,00E+00	1,3	1,31E+03	1,31E+03	3,05E+01	2,08E+02	2,93E+00	2,25E-03	1419,614	21	1,00E+00	1,3	1,31E+03
1469,915	21	1,00E+00	1,3	1,31E+03	1,31E+03	2,91E+01	2,09E+02	3,49E+00	2,68E-03	1469,915	21	1,00E+00	1,3	1,31E+03
1521,166	20,9	1,00E+00	1,2	1,31E+03	1,31E+03	2,80E+01	2,09E+02	4,17E+00	3,20E-03	1521,166	20,9	1,00E+00	1,2	1,31E+03
1572,167	21	1,00E+00	1,2	1,31E+03	1,31E+03	2,76E+01	2,09E+02	4,98E+00	3,82E-03	1572,167	21	1,00E+00	1,2	1,31E+03
1623,45	21	1,00E+00	1,2	1,31E+03	1,31E+03	2,83E+01	2,09E+02	5,95E+00	4,56E-03	1623,45	21	1,00E+00	1,2	1,31E+03
1673,681	21	1,00E+00	1,2	1,31E+03	1,31E+03	2,86E+01	2,09E+02	7,10E+00	5,44E-03	1673,681	21	1,00E+00	1,2	1,31E+03
1724,495	20,9	1,00E+00	1,2	1,31E+03	1,31E+03	2,76E+01	2,09E+02	8,47E+00	6,49E-03	1724,495	20,9	1,00E+00	1,2	1,31E+03
1774,488	21	1,00E+00	1,2	1,31E+03	1,31E+03	2,70E+01	2,09E+02	1,01E+01	7,75E-03	1774,488	21	1,00E+00	1,2	1,31E+03
1824,695	21	1,00E+00	1,2	1,32E+03	1,32E+03	2,70E+01	2,10E+02	1,21E+01	9,23E-03	1824,695	21	1,00E+00	1,2	1,32E+03
1874,745	21	1,00E+00	1,2	1,32E+03	1,32E+03	2,69E+01	2,09E+02	1,44E+01	1,10E-02	1874,745	21	1,00E+00	1,2	1,32E+03
1925,538	21	1,00E+00	1,2	1,32E+03	1,32E+03	2,70E+01	2,10E+02	1,72E+01	1,32E-02	1925,538	21	1,00E+00	1,2	1,32E+03
1975,536	20,9	1,00E+00	1,2	1,32E+03	1,32E+03	2,72E+01	2,10E+02	2,06E+01	1,57E-02	1975,536	20,9	1,00E+00	1,2	1,32E+03
2025,378	21	1,00E+00	1,1	1,32E+03	1,32E+03	2,60E+01	2,10E+02	2,45E+01	1,87E-02	2025,378	21	1,00E+00	1,1	1,32E+03
2075,792	21	1,00E+00	1,2	1,32E+03	1,32E+03	2,69E+01	2,10E+02	2,93E+01	2,24E-02	2075,792	21	1,00E+00	1,2	1,32E+03
2126,334	21	1,00E+00	1,1	1,32E+03	1,32E+03	2,63E+01	2,10E+02	3,50E+01	2,67E-02	2126,334	21	1,00E+00	1,1	1,32E+03
2176,663	21	1,00E+00	1,2	1,32E+03	1,32E+03	2,68E+01	2,09E+02	4,18E+01	3,19E-02	2176,663	21	1,00E+00	1,2	1,32E+03
2226,967	21	1,00E+00	1,1	1,31E+03	1,31E+03	2,60E+01	2,09E+02	4,99E+01	3,82E-02	2226,967	21	1,00E+00	1,1	1,31E+03
2277,775	21	1,00E+00	1,1	1,31E+03	1,31E+03	2,63E+01	2,09E+02	5,96E+01	4,56E-02	2277,775	21	1,00E+00	1,1	1,31E+03
2328,075	21,1	1,00E+00	1,1	1,31E+03	1,31E+03	2,56E+01	2,09E+02	7,11E+01	5,46E-02	2328,075	21,1	1,00E+00	1,1	1,31E+03
2378,859	21	1,00E+00	1,1	1,31E+03	1,31E+03	2,53E+01	2,08E+02	8,49E+01	6,53E-02	2378,859	21	1,00E+00	1,1	1,31E+03
2429,03	21	1,00E+00	1,1	1,30E+03	1,30E+03	2,59E+01	2,07E+02	1,01E+02	7,83E-02	2429,03	21	1,00E+00	1,1	1,30E+03
2479,641	21	1,00E+00	1,1	1,30E+03	1,30E+03	2,51E+01	2,06E+02	1,21E+02	9,39E-02	2479,641	21	1,00E+00	1,1	1,30E+03
2529,793	21	1,00E+00	1,1	1,29E+03	1,29E+03	2,46E+01	2,05E+02	1,44E+02	1,13E-01	2529,793	21	1,00E+00	1,1	1,29E+03
2579,946	21	1,00E+00	1,1	1,28E+03	1,28E+03	2,51E+01	2,04E+02	1,72E+02	1,36E-01	2579,946	21	1,00E+00	1,1	1,28E+03

2630,483	21	1,00E+00	1,1	1,27E+03	1,27E+03	2,53E+01	2,02E+02	2,06E+02	1,63E-01	2630,483	21	1,00E+00	1,1	1,27E+03
2680,262	20,9	1,00E+00	1,1	1,26E+03	1,26E+03	2,45E+01	2,01E+02	2,46E+02	1,96E-01	2680,262	20,9	1,00E+00	1,1	1,26E+03
2730,483	21	1,00E+00	1,1	1,26E+03	1,26E+03	2,48E+01	2,00E+02	2,93E+02	2,35E-01	2730,483	21	1,00E+00	1,1	1,26E+03
2780,416	20,9	1,00E+00	1,1	1,26E+03	1,26E+03	2,48E+01	2,00E+02	3,50E+02	2,81E-01	2780,416	20,9	1,00E+00	1,1	1,26E+03
2830,442	21	1,00E+00	1,2	1,26E+03	1,26E+03	2,57E+01	2,00E+02	4,18E+02	3,35E-01	2830,442	21	1,00E+00	1,2	1,26E+03
2880,416	21	1,00E+00	1,2	1,25E+03	1,25E+03	2,56E+01	2,00E+02	4,99E+02	4,01E-01	2880,416	21	1,00E+00	1,2	1,25E+03
2930,341	21	1,00E+00	1,2	1,25E+03	1,25E+03	2,68E+01	1,99E+02	5,96E+02	4,80E-01	2930,341	21	1,00E+00	1,2	1,25E+03
2980,384	21	1,00E+00	1,4	1,25E+03	1,25E+03	2,97E+01	1,99E+02	7,12E+02	5,74E-01	2980,384	21	1,00E+00	1,4	1,25E+03
3030,329	21	1,00E+00	2,1	1,22E+03	1,22E+03	4,51E+01	1,94E+02	8,50E+02	7,01E-01	3030,329	21	1,00E+00	2,1	1,22E+03
3080,414	21	1,00E+00	5,2	1,07E+03	1,07E+03	9,66E+01	1,70E+02	1,01E+03	9,55E-01	3080,414	21	1,00E+00	5,2	1,07E+03
3130,228	21	1,00E+00	86	5,57E+01	3,84E+00	5,56E+01	8,86E+00	1,21E+03	2,13E+01	3130,228	21	1,00E+00	86	5,57E+01
3180,07	21,1	1,00E+00	84,6	9,92E-01	9,40E-02	9,87E-01	1,58E-01	1,45E+03	1,75E+02	3180,07	21,1	1,00E+00	84,6	9,92E-01
3229,992	21,1	1,00E+00	12,6	2,16E+00	2,11E+00	4,72E-01	3,44E-01	1,73E+03	1,65E+02	3229,992	21,1	1,00E+00	12,6	2,16E+00
3279,778	21	1,00E+00	6,1	5,46E+00	5,42E+00	5,82E-01	8,68E-01	2,06E+03	1,50E+02	3279,778	21	1,00E+00	6,1	5,46E+00
3329,638	21	1,00E+00	4,2	9,58E+00	9,56E+00	7,01E-01	1,53E+00	2,46E+03	1,38E+02	3329,638	21	1,00E+00	4,2	9,58E+00
3379,531	21,1	1,00E+00	3,3	1,40E+01	1,40E+01	8,05E-01	2,23E+00	2,94E+03	1,32E+02	3379,531	21,1	1,00E+00	3,3	1,40E+01
3429,346	21,1	1,00E+00	2,6	1,83E+01	1,83E+01	8,43E-01	2,92E+00	3,51E+03	1,32E+02	3429,346	21,1	1,00E+00	2,6	1,83E+01
3479,071	21	1,00E+00	2,3	2,26E+01	2,25E+01	8,94E-01	3,59E+00	4,19E+03	1,36E+02	3479,071	21	1,00E+00	2,3	2,26E+01
3529,271	21	1,00E+00	2,3	2,84E+01	2,84E+01	1,15E+00	4,53E+00	5,00E+03	1,36E+02	3529,271	21	1,00E+00	2,3	2,84E+01

Frequency sweep

Fresh gel

Time *s*	Temp. *°C*	Freq. *Hz*	Complex Modulus *Pa*	Elastic Modulus *Pa*	Viscous Modulus *Pa*	Complex Viscosity *Pas*	Phase Angle *°*	Shear Stress *Pa*	Strain	Acc. Time *s*	Ang. Freq. *rad/s*	Torque *Nm*	Eta Double Prime *Pas*	Dyn. Visc. *Pas*
134	21	100	6.708E4	9972	6.633E4	106.8	81.45	1.764E4	0.07102	134	628.3	0.07217	15.87	105.6
268.6	21.1	100	6.618E4	5612	6.594E4	105.3	85.13	9100	0.03604	268.6	628.3	0.03723	8.932	104.9
402.5	21.1	75	2.739E4	7687	2.629E4	58.12	73.7	1.769E4	0.1177	402.5	471.2	0.07235	16.31	55.79
536.9	21	60	1.389E4	5267	1.285E4	36.84	67.71	2.287E4	0.2384	536.9	377	0.09354	13.97	34.09
671.1	20.9	50	8396	4060	7350	26.73	61.08	1.987E4	0.2974	671.1	314.2	0.08128	12.92	23.39
805.3	21.1	42.86	6042	3412	4986	22.44	55.62	1.404E4	0.2838	805.3	269.3	0.05743	12.67	18.52
942	21	37.5	3.778E10	2.454E10	2.872E10	1.603E8	49.48	2.297E4	6.081E-7	942	235.6	0.09397	1.042E8	1.219E8
1076	21	30	6.847E4	6.639E4	1.677E4	363.3	14.18	2.062E4	0.2281	1076	188.5	0.08433	352.2	88.97
1209	21.1	25	6.967E4	6.908E4	9056	443.5	7.468	2.099E4	0.2465	1209	157.1	0.08584	439.8	57.65
1290	21.2	21.43	674.1	556.9	379.8	5.007	34.29	5999	0.4993	1290	134.6	0.02454	4.136	2.821
1423	21	17.65	410.5	236.3	335.7	3.702	54.86	4242	0.5296	1423	110.9	0.01735	2.131	3.028
1557	21	14.29	167.3	23.88	165.5	1.863	81.79	3444	0.6796	1557	89.76	0.01409	0.266	1.844
1611	21	12	69.21	14.42	67.69	0.9179	77.98	1811	0.5022	1611	75.4	0.007408	0.1912	0.8977
1745	21	10	44.12	36.24	25.15	0.7021	34.76	1167	0.4748	1745	62.83	0.004773	0.5768	0.4003
1798	21.1	8.571	141	117.2	78.32	2.618	33.75	847.7	0.4938	1798	53.86	0.003468	2.177	1.454
1933	21	7.143	136.8	119.5	66.64	3.049	29.15	705.5	0.611	1933	44.88	0.002886	2.663	1.485
2014	21	5.882	116.1	87.45	76.31	3.14	41.11	390.8	0.5015	2014	36.96	0.001598	2.366	2.065
2148	20.9	5	157.4	131.7	86.34	5.011	33.26	267.6	0.536	2148	31.42	0.001095	4.191	2.748
2256	21	4.167	185.6	153.7	104.1	7.091	34.12	150.3	0.5042	2256	26.18	0.0006147	5.87	3.977
2394	20.9	3.488	239.1	223.4	85.28	10.91	20.89	43.7	0.3736	2394	21.92	0.0001788	10.19	3.891

2450	21.1	2.913	232.8	211.5	97.28	12.72	24.7	48.1	0.4945	2450	18.3	0.0001968	11.56	5.316
2508	21.1	2.439	250.3	233.3	90.69	16.33	21.24	61.16	0.4923	2508	15.32	0.0002502	15.22	5.918
2654	21	2.041	305.8	299.5	61.53	23.85	11.61	83.84	0.4087	2654	12.82	0.0003429	23.36	4.798
2714	21	1.705	317.8	311.6	62.31	29.67	11.31	122.1	0.4942	2714	10.71	0.0004996	29.09	5.818
2806	21.1	1.429	336.7	331.5	58.68	37.51	10.04	141.3	0.493	2806	8.976	0.0005782	36.93	6.537
2902	21.1	1.195	355.1	351.3	52.31	47.29	8.471	157.8	0.4931	2902	7.51	0.0006454	46.77	6.966
3001	21.1	1	371	367.5	50.87	59.05	7.88	172.6	0.4982	3001	6.283	0.0007059	58.49	8.096
3054	20.9	0.838	376.2	372.9	49.69	71.45	7.591	177.1	0.4934	3054	5.265	0.0007243	70.82	9.438
3107	21	0.7026	383.7	380.4	50.47	86.93	7.557	182.8	0.4921	3107	4.414	0.0007478	86.17	11.43
3160	21	0.5882	388.1	384.8	50.26	105	7.441	187.6	0.4942	3160	3.696	0.0007673	104.1	13.6
3187	21	0.4926	388.3	385	51.1	125.5	7.561	187.6	0.4907	3187	3.095	0.0007675	124.4	16.51
3246	21	0.4127	393	389.6	51.47	151.6	7.527	191.9	0.4937	3246	2.593	0.0007851	150.2	19.85
3280	21	0.3456	393.1	389.7	51.64	181	7.549	191.9	0.492	3280	2.172	0.0007851	179.4	23.78
3355	21.1	0.2896	399.9	396.5	51.56	219.8	7.409	196	0.4927	3355	1.819	0.0008018	217.9	28.34
3399	21	0.2425	401.5	398.1	51.79	263.5	7.412	196	0.49	3399	1.524	0.0008018	261.3	33.99
3498	20.9	0.2031	410.9	407.6	51.88	322	7.254	201.6	0.4917	3498	1.276	0.0008245	319.4	40.65
3612	21.1	0.1702	421.9	418.7	51.74	394.6	7.044	206.9	0.4912	3612	1.069	0.0008462	391.6	48.39
3745	21	0.1425	434.3	431.3	51.29	485	6.782	212.8	0.4906	3745	0.8955	0.0008706	481.6	57.27
3899	20.9	0.1194	448.6	445.8	50.58	598.1	6.473	219.9	0.4906	3899	0.7501	0.0008997	594.3	67.43

Rehydrated gel

Time s	Temp °C	Freq Hz	Complex Modulus Pa	Elastic Modulus Pa	Viscous Modulus Pa	Complex Viscosity Pas	Phase Angle °	Shear Stress Pa	Strain
401.801	21	7.50E+01	84.5	7.72E+03	7.40E+02	7.68E+03	1.64E+01	1.47E+04	3.16E-01
535.646	21.1	6.00E+01	80.6	3.50E+03	5.75E+02	3.46E+03	9.29E+00	1.78E+04	6.01E-01
670.479	21	5.00E+01	52.4	2.10E+03	1.28E+03	1.67E+03	6.69E+00	3.45E+03	1.76E-01
805.045	21	4.29E+01	37.8	1.42E+03	1.12E+03	8.68E+02	5.26E+00	4.85E+03	3.42E-01
938.732	20.7	3.75E+01	51.9	4.21E+02	2.59E+02	3.31E+02	1.79E+00	9.93E+03	8.68E-01
1073.089	21	3.00E+01	3.28E-02	8.11E+02	8.11E+02	4.64E-01	4.30E+00	2.95E+03	4.43E-01
1207.315	21.2	2.50E+01	24	5.03E+02	4.60E+02	2.05E+02	3.20E+00	2.82E+03	5.95E-01
1341.542	20.9	2.14E+01	27.4	5.90E+02	5.24E+02	2.71E+02	4.38E+00	1.65E+03	5.01E-01
1476.224	21	1.76E+01	31.9	5.69E+02	4.83E+02	3.01E+02	5.13E+00	1.15E+03	5.41E-01
1610.159	21	1.43E+01	34.7	6.14E+02	5.05E+02	3.49E+02	6.84E+00	5.71E+02	4.60E-01
1744.174	20.9	1.20E+01	33.9	5.64E+02	4.68E+02	3.15E+02	7.48E+00	4.77E+02	6.00E-01
1878.167	21.1	1.00E+01	35.2	5.86E+02	4.79E+02	3.38E+02	9.33E+00	2.77E+02	5.67E-01
2012.45	21	8.57E+00	36.2	5.62E+02	4.54E+02	3.32E+02	1.04E+01	1.88E+02	5.13E-01
2146.992	21	7.14E+00	34	6.47E+02	5.36E+02	3.61E+02	1.44E+01	1.76E+02	4.65E-01
2281.327	21	5.88E+00	33	6.59E+02	5.53E+02	3.59E+02	1.78E+01	1.98E+02	4.43E-01
2415.028	21	5.00E+00	31.8	6.86E+02	5.83E+02	3.62E+02	2.18E+01	2.10E+02	4.03E-01
2550.573	21	4.17E+00	33.8	6.64E+02	5.52E+02	3.69E+02	2.53E+01	2.31E+02	4.20E-01
2688.27	21	3.49E+00	34.7	6.34E+02	5.21E+02	3.62E+02	2.89E+01	2.43E+02	4.39E-01
2827.381	21	2.91E+00	36.3	5.93E+02	4.77E+02	3.51E+02	3.24E+01	2.49E+02	4.64E-01
2912.618	21	2.44E+00	37.2	5.44E+02	4.33E+02	3.29E+02	3.55E+01	2.55E+02	5.04E-01
3057.632	21.1	2.04E+00	36.2	5.42E+02	4.37E+02	3.20E+02	4.23E+01	2.57E+02	4.99E-01
3177.278	21	1.70E+00	36	5.27E+02	4.26E+02	3.09E+02	4.92E+01	2.58E+02	5.08E-01

3300.449	21	1.43E+00	35.6	5.19E+02	4.22E+02	3.02E+02	5.78E+01	2.55E+02	5.05E-01
3427.292	21	1.20E+00	35.6	5.08E+02	4.13E+02	2.96E+02	6.76E+01	2.52E+02	5.05E-01
3559.238	21	1.00E+00	35.3	4.99E+02	4.07E+02	2.89E+02	7.95E+01	2.48E+02	5.03E-01
3665.689	21	8.38E-01	35.2	4.89E+02	3.99E+02	2.82E+02	9.28E+01	2.43E+02	5.03E-01
3745.588	21	7.03E-01	34.9	4.86E+02	3.98E+02	2.78E+02	1.10E+02	2.37E+02	4.91E-01
3825.111	21	5.88E-01	34.9	4.73E+02	3.88E+02	2.71E+02	1.28E+02	2.32E+02	4.93E-01
3904.894	20.9	4.93E-01	34.6	4.65E+02	3.83E+02	2.64E+02	1.50E+02	2.29E+02	4.93E-01
3993.522	21	4.13E-01	34.4	4.56E+02	3.77E+02	2.58E+02	1.76E+02	2.25E+02	4.94E-01
4093.449	21	3.46E-01	34	4.50E+02	3.73E+02	2.52E+02	2.07E+02	2.22E+02	4.93E-01
4206.817	21	2.90E-01	33.6	4.45E+02	3.70E+02	2.46E+02	2.44E+02	2.19E+02	4.93E-01
4249.952	21	2.43E-01	33.2	4.30E+02	3.60E+02	2.35E+02	2.82E+02	2.19E+02	5.10E-01
4398.572	21.1	2.03E-01	32.6	4.37E+02	3.69E+02	2.35E+02	3.43E+02	2.14E+02	4.91E-01
4455.738	21	1.70E-01	32.1	4.28E+02	3.63E+02	2.28E+02	4.01E+02	2.14E+02	5.01E-01
4522.014	21	1.43E-01	31.6	4.22E+02	3.60E+02	2.21E+02	4.71E+02	2.14E+02	5.08E-01
4830.594	21	1.19E-01	30.4	4.29E+02	3.70E+02	2.18E+02	5.72E+02	2.17E+02	5.07E-01
4920.707	21	1.00E-01	30	4.29E+02	3.71E+02	2.14E+02	6.82E+02	2.17E+02	5.07E-01

Density measurements

Marks and Spencer Gelatine sheet

Mass (g)	0.8610
Area (cm²)	34.68
Volume (cm³)	0.667012

	Thickness (mm)	Volume (cm³)	SD, Volume
	0.193	0.669324	
	0.197	0.683196	
	0.193	0.669324	
	0.193	0.669324	
	0.194	0.672792	
	0.191	0.662388	
	0.190	0.658920	
	0.191	0.662388	
	0.189	0.655452	
Mean:	0.192333	0.667012	0.008316

Given a 95% confidence interval of the volume

$$V = 0.667012 \pm \frac{1.96 \cdot 0.008316}{\sqrt{9}}\, ml = 0.667012 \pm 0.005433\, ml$$

which results in the density being

$$\rho = (1.280402, 1.301432)\, g/ml = 1290.9 \pm 10.5\, kg/m^3$$

Very dry piece of film

Mass (g)	0,0967
Area (cm²)	9,144576
Volume (cm³)	0,0759
Density (g/ml)	1,274045

	Height (mm)
	0,084
	0,083
	0,080
	0,083
	0,085
	0,092
	0,090
	0,084
	0,081
	0,082
	0,081
	0,084
	0,078
	0,077
	0,081
Mean:	0,0830

The density is

$$\rho = 1274.0\, kg/m^3$$

NB! Please note that there is no meaningful way to give an estimate of the error of measurement due to the sample's ski-sloped shaped geometry.

Gelatine solution

Data from 20/5 (g)	4.87	4.90	4.89	4.96	4.87	4.91	4.87	4.85
Data from 26/5 (g)	4.87	4.87	4.88	4.89	4.86	4.91	4.88	4.85
Data from 27/5 (g)	4.89	4.86	4.88	4.81	4.88	4.79	4.85	4.89

Sum (g)	Mean (g)	SD
107.38	4.877143	0.017928

Given a 95% confidence interval of the weight (excluding marked data)

$$m = 4.877143 \pm \frac{1.96 \cdot 0.017928}{\sqrt{21}} g = 4.877143 \pm 0.0076681 g$$

which results of the density being, given a 5.00 ml volume

$$\rho = (0.97389, 0.97696) g/ml = 975.4 \pm 1.6 kg/m^3$$

Pipette accuracy

2 ml with plastic pipette

2 ml with a plastic pipette was put on a scale and measured the mass increase.

Series 1	Added:	Series 2	Added:	Series 3	Added:
1.82	1.82	1.76	1.76	1.84	1.84
3.63	1.81	3.54	1.78	3.65	1.81
5.28	1.65	5.34	1.80	5.45	1.80
7.00	1.72	7.18	1.84	7.30	1.85
8.81	1.81	8.97	179	9.14	1.84
11.57	1.76	10.80	1.83	10.98	1.84
12.39	1.82	12.57	1.77	12.76	1.78

Mean	SD
1.79619	0.05249

Given a 95% confidence interval of the mass

$$m = 1.796916 \pm \frac{1.96 \cdot 0.05249}{\sqrt{21}} g = 1.7962 \pm 0.0225 g$$

which given the density for water at 20 °C being 998.2 kg/m^3 results in the volume $V = (1.7771, 1.8\,218) ml = 1.7994 \pm 0.0223 ml$.

This is 90.0% of the claimed volume.

3 ml with plastic pipette

3 ml with a plastic pipette was put on a scale and measured the mass increase.

Series 1	Added:	Series 2	Added:	Series 3	Added:	Series 4	Added:
2.72	2.72	2.76	2.76	2.72	2.72	2.72	2.72
5.45	2.73	5.50	2.74	5.38	2.66	5.38	2.66
8.19	2.74	8.27	2.77	8.10	2.72	8.09	2.71
10.87	2.68	10.96	2.69	10.85	2.75	10.77	2.68
13.62	2.75	13.70	2.74	13.54	2.69	13.49	2.72

Mean	SD
2.7175	0.031933

Given a 95% confidence interval of the mass

$$m = 2.7175 \pm \frac{1.96 \cdot 0.031993}{\sqrt{20}} g = 2.7175 \pm 0.0140 g$$

which given the density for water at 20 °C being 998.2 kg/m^3 results in the volume

$$V = \left(2.7084, 2.7\,364\right) ml = 2.7224 \pm 0.0140 ml\,.$$

This is 90.7% of the claimed volume.

5 ml glass pipette

5 ml with a glass pipette was put on a scale and measured the mass increase.

Series	Added	
4.99	4.99	
9.97	4.98	
14.97	5.00	
19.98	5.01	
24.99	5.01	
29.98	4.99	
34.99	5.01	
40.01	5.02	
45.00	4.99	
50.00	5.00	SD
Mean:	5.0000	0.012472

Given a 95% confidence interval of the mass

$$m = 5.0000 \pm \frac{1.96 \cdot 0.012742}{\sqrt{10}} g = 5.0000 \pm 0.0077 g$$

which given the density for water at 20 °C being 998.2 kg/m^3 results in the volume

$$V = \left(5.0013, 5.0\,17\right) ml = 5.0090 \pm 0.0077 ml$$

This is 100,2% of the claimed volume, and also note that this is within the specified tolerance of the scale.

Kinetics experiments

Swelling dried gelatine film at 21 °C, made from 1.8 ml gel

Gravimetric experiment.

	Time (h)	Mass, tot 1	Mass, tot 2	Mass, tot 3	Mass, tot avg (g)	Mass, gel 1 (g)	Mass, gel 2 (g)	Mass, gel 3 (g)	Mass, gel, avg (g)
Dry	0	14,4	14,48	14,4	14,42667	0,11	0,12	0,11	0,113333
Wet	0	14,52	14,6	14,52	14,54667	0,23	0,24	0,23	0,233333
Wet	0,25	14,92	15,05	14,91	14,96	0,63	0,69	0,62	0,646667
Wet	0,5	15,07	15,14	15,06	15,09	0,78	0,78	0,77	0,776667
Wet	0,75	15,15	15,22	15,13	15,16667	0,86	0,86	0,84	0,853333
Wet	1	15,22	15,27	15,18	15,22333	0,93	0,91	0,89	0,91
Wet	1,25	15,23	15,28	15,22	15,24333	0,94	0,92	0,93	0,93
Wet	1,5	15,26	15,32	15,24	15,27333	0,97	0,96	0,95	0,96
Wet	2	15,28	15,37	15,26	15,30333	0,99	1,01	0,97	0,99
Wet	3	15,33	15,41	15,29	15,34333	1,04	1,05	1	1,03
Wet	4	15,36	15,39	15,32	15,35667	1,07	1,03	1,03	1,043333
Wet	5	15,39	15,42	15,33	15,38	1,1	1,06	1,04	1,066667
Wet	6	15,4	15,41	15,34	15,38333	1,11	1,05	1,05	1,07
Wet	7	15,38	15,45	15,36	15,39667	1,09	1,09	1,07	1,083333
Wet	8	15,42	15,44	15,36	15,40667	1,13	1,08	1,07	1,093333
Wet	24	15,48	15,49	15,42	15,46333	1,19	1,13	1,13	1,15

The stainless steel discs measured 14.29g, 14.36g and 14,29g respectively.

Swelling dried gelatine film at 21 °C, made from 4.2 ml gel

Gravimetric experiment, no 1.

	Time (h)	Mass 1 (g)	Mass 2 (g)	Mass 3 (g)	Mass avg (g)	Mass, gel 1 (g)	Mass, gel 2 (g)	Mass, gel 3 (g)	Mass, gel, avg (g)
Dry	0	14,63	14,63	14,65	14,63667	0,26	0,25	0,24	0,25
Wet	0	14,76	14,75	14,76	14,75667	0,39	0,37	0,35	0,37
Wet	0,25	15,49	15,44	15,46	15,46333	1,12	1,06	1,05	1,076667
Wet	0,5	15,83	15,73	15,78	15,78	1,46	1,35	1,37	1,393333
Wet	1	16,07	16,05	16,1	16,07333	1,7	1,67	1,69	1,686667
Wet	1,5	16,24	16,26	16,29	16,26333	1,87	1,88	1,88	1,876667
Wet	2	16,36	16,4	16,43	16,39667	1,99	2,02	2,02	2,01
Wet	2,5	16,48	16,52	16,58	16,52667	2,11	2,14	2,17	2,14
Wet	3	16,57	16,58	16,67	16,60667	2,2	2,2	2,26	2,22
Wet	3,25	16,6	16,63	16,71	16,64667	2,23	2,25	2,3	2,26
Wet	3,5	16,62	16,67	16,73	16,67333	2,25	2,29	2,32	2,286667
Wet	3,75	16,64	16,7	16,77	16,70333	2,27	2,32	2,36	2,316667
Wet	4	16,68	16,7	16,79	16,72333	2,31	2,32	2,38	2,336667
Wet	4,25	16,66	16,72	16,81	16,73	2,29	2,34	2,4	2,343333
Wet	4,5	16,67	16,75	16,8	16,74	2,3	2,37	2,39	2,353333

Wet	5	16,73	16,79	16,86	16,79333	2,36	2,41	2,45	2,406667
Wet	5,25	16,7	16,78	16,86	16,78	2,33	2,4	2,45	2,393333
Wet	23	16,97	17,02	17,19	17,06	2,6	2,64	2,78	2,673333
Wet	27,5	17,01	17,06	17,22	17,09667	2,64	2,68	2,81	2,71

The stainless steel discs measured 14.37g, 14.38g and 14.41g respectively.

Gravimetric experiment, no 2.

Time (min)	Time (h)	Mass 1, tot (g)	Mass 2, tot (g)	Mass 3, tot (g)	Mass 1, gel (g)	Mass 2, gel (g)	Mass 3, gel (g)
0	0	14,61	14,53	14,6	0,29	0,25	0,25
0	0	14,75	14,65	14,75	0,43	0,37	0,4
2	0,033333			15,04			0,69
4	0,066667	15,08	15,01	15,12	0,76	0,73	0,77
6	0,1			15,26			0,91
8	0,133333	15,25	15,17	15,36	0,93	0,89	1,01
10	0,166667			15,43			1,08
12	0,2	15,4	15,3	15,51	1,08	1,02	1,16
14	0,233333			15,57			1,22
16	0,266667	15,51	15,41	15,61	1,19	1,13	1,26
18	0,3			15,66			1,31
20	0,333333	15,6	15,5	15,68	1,28	1,22	1,33
22	0,366667			15,77			1,42
24	0,4	15,69	15,59	15,81	1,37	1,31	1,46
26	0,433333			15,84			1,49
28	0,466667	15,79	15,66	15,89	1,47	1,38	1,54
30	0,5			15,92			1,57
32	0,533333	15,85	15,72	15,96	1,53	1,44	1,61
34	0,566667			16,01			1,66
36	0,6	15,89	15,75	16,02	1,57	1,47	1,67
38	0,633333			16,05			1,7
40	0,666667	15,94	15,82	16,09	1,62	1,54	1,74
44	0,733333	16,02	15,89		1,7	1,61	
48	0,8	16,09	15,92		1,77	1,64	
52	0,866667	16,12	15,96		1,8	1,68	
56	0,933333	16,17	16,02		1,85	1,74	
60	1	16,21	16,08		1,89	1,8	

The stainless steel discs measured 14.32g, 14.28g and 14.35g respectively.

Swelling dried gelatine film at 21 °C, made from 5 ml gel

Gravimetric experiment.

Time (h)	Raw data Sample no 1	2	3	4		Amount of imbibed solvent (g) Sample no 1	2	3	4	Mean	SD	dW/dt	φ_w
					Disc	14.08	14.24	14.16	14.25				
0	14.38	14.56	14.46	14.55	Film	0.30	0.32	0.30	0.30	0.305	0.01		
0	14.46	14.62	14.56	14.64	Water layer	0.08	0.06	0.10	0.09	0.0825	0.017078		
0.083333	14.87	15.02	14.94	15.04	Solvent imbibed	0.41	0.40	0.38	0.40	0.3975	0.012583	4.77	0.62454
0.166667	15.06	15.23	15.13	15.24		0.60	0.61	0.57	0.60	0.595	0.017321	2.37	0.71345
0.25	15.22	15.38	15.27	15.38		0.76	0.76	0.71	0.74	0.7425	0.023629	1.77	0.75652
0.333333	15.33	15.48	15.40	15.47		0.87	0.86	0.84	0.83	0.85	0.018257	1.29	0.78055
0.416667	15.42	15.58	15.49	15.60		0.96	0.96	0.93	0.96	0.9525	0.015	1.23	0.79943
0.5	15.49	15.68	15.58	15.70		1.03	1.06	1.02	1.06	1.0425	0.020616	1.08	0.81352
0.583333	15.59	15.76	15.66	15.78		1.13	1.14	1.10	1.14	1.1275	0.01893	1.02	0.82512
0.666667	15.64	15.82	15.74	15.85		1.18	1.20	1.18	1.21	1.1925	0.015	0.78	0.83306
0.833333	15.76	15.97	15.88	15.97		1.30	1.35	1.32	1.33	1.325	0.020817	0.795	0.84720
1	15.86	16.05	15.95	16.08		1.40	1.43	1.39	1.44	1.415	0.023805	0.54	0.85552
1.25	15.99	16.18	16.11	16.20		1.53	1.56	1.55	1.56	1.55	0.014142	0.54	0.86642
1.5	16.09	16.30	16.18	16.31		1.63	1.68	1.62	1.67	1.65	0.029439	0.4	0.87349
1.75	16.19	16.39	16.28	16.43		1.73	1.77	1.72	1.79	1.7525	0.03304	0.41	0.88000
2	16.30	16.47	16.37	16.54		1.84	1.85	1.81	1.90	1.85	0.037417	0.39	0.88560
2.5	16.45	16.61	16.53	16.67		1.99	1.99	1.97	2.03	1.995	0.025166	0.29	0.89303
3	16.56	16.76	16.65	16.83		2.10	2.14	2.09	2.19	2.13	0.045461	0.27	0.89912
3.5	16.68	16.84	16.75	16.93		2.22	2.22	2.19	2.29	2.23	0.042426	0.2	0.90321
4	16.79	16.96	16.85	17.05		2.33	2.34	2.29	2.41	2.3425	0.049917	0.225	0.90743
4.583333	16.92	17.06	16.96	17.13		2.46	2.44	2.40	2.49	2.4475	0.037749	0.18	0.91105
5	16.97	17.15	17.04	17.23		2.51	2.53	2.48	2.59	2.5275	0.046458	0.192	0.91362
5.5	17.06	17.27	17.08	17.31		2.60	2.65	2.52	2.67	2.61	0.066833	0.165	0.91612
6	17.13	17.35	17.18	17.40		2.67	2.73	2.62	2.76	2.695	0.06245	0.17	0.91855
23.58333	18.15	18.33	18.16	18.51		3.69	3.71	3.60	3.87	3.7175	0.112361	0.058152	0.93960
25	18.23	18.35	18.20	18.52		3.77	3.73	3.64	3.88	3.755	0.099499	0.026471	0.94017
29.66667	18.39	18.46	18.28	18.62		3.93	3.84	3.72	3.98	3.8675	0.114127	0.024107	0.94181
48.58333	18.75	18.84	18.56	18.93		4.29	4.22	4.00	4.29	4.2	0.137356	0.017577	0.94616
51.58333	18.77	18.90	18.57	18.94		4.31	4.28	4.01	4.30	4.225	0.143875	0.008333	0.94647
75.41667	18.75	18.95	18.71	19.01		4.29	4.33	4.15	4.37	4.285	0.095743	0.002517	0.94718
100.3333	18.81	19.16	18.85	19.07		4.35	4.54	4.29	4.43	4.4025	0.108128	0.004716	0.94851
120.9167	18.83	19.21	18.93	19.09		4.37	4.59	4.37	4.45	4.445	0.103763	0.002065	0.94898
144.25	18.87	19.29	18.94	19.11		4.41	4.67	4.38	4.47	4.4825	0.13048	0.001607	0.94939
167.9167	18.79	19.14	18.88	18.96		4.33	4.52	4.32	4.32	4.3725	0.098446	-0.00465	0.94818

Fluid dynamic gauging

z (mm)	t (h)	t_1 (s)	m_1 (g)	t_2 (s)	m_2 (g)
20	0,108333	10	51,78	10,16	47,11
20	0,141667	9,97	57,66	9,97	43,96
20	0,176389	10,17	63,06	9,88	57,99
20	0,204167	9,99	67,98	9,87	62,33
20	0,230556	9,77	71,13	9,97	66,03
19,8	0,263889	10,29	78,46	9,96	73,14
19,8	0,290278	10,26	85,46	10	80,12
19,8	0,316667	10,12	92,2	9,88	86,73

19,8	0,35	10,16	98,63	9,97	93,03
19,8	0,375	10,27	104,7	10,25	99
19,8	0,395833	10,17	110,49	9,93	104,63
19,8	0,430556	10,22	50,31	10,31	45,6
19,8	0,456944	10,15	55,1	9,88	50,3
19,8	0,483333	11,18	60,02	10,37	54,81
19,6	0,5875	10,04	66,98	9,97	61,92
19,6	0,670833	10,14	73,58	9,87	68,34
19,6	0,745833	10,06	79,95	9,88	74,29
19,6	0,833333	10,06	84,66	10,34	79,64
19,5	0,9125	10,41	91,44	10,34	86,39
19,5	1	10,08	97,3	10,19	92,38
19,5	1,25	9,97	101,05	9,87	96,17
19,4	1,495833	10,44	49,8	10,04	44,67
19,4	1,745833	10,39	52,05	10,53	46,95
19,3	1,991667	10,18	55,75	10	50,46
19,2	2,245833	10,14	60,59	10,06	55,27
19,2	2,511111	10,29	63,91	10,16	58,4
19,1	2,741667	10,07	68,7	10,06	63,24
19,1	2,995833	10,02	72,26	10,16	66,9
19	3,241667	10,33	77,65	10,13	72,32
19	3,495833	10,07	81,85	10,13	76,52
18,9	3,7375	10,26	87,65	10,35	82,52
18,9	4,008333	10,03	94,17	10,03	87,42
18,9	4,2625	10,27	49,2	9,75	44,11
18,8	4,4875	9,97	54,58	10,28	49,61
18,8	4,766667	9,91	59,41	10,41	54,16
18,8	4,991667	10,03	63,41	10,03	58,25
16,7	21,49583	10,04	53,52	9,97	48,57
17,2	22,04583	10,03	70,25	9,9	65,18
17,5	22,11667	9,94	78,31	10,15	73,45
17,6	22,15	10,29	86,28	10,69	81,72
16,7	70,9375	10,13	53,15	10,1	48,4
17	70,79861	9,97	60,76	9,91	56,15
5	70,83333	10,81	69,22	10,07	64,06

z_0 (mm) 23,10

Disc+gel 14,64 Disc (g) 14,30

The hydrostatic head was kept at 90mm.

Swelling dried gelatine film at 21 °C, made from 7.2 ml gel

Gravimetric experiment.

Time	Sample 1	Sample 2	Sample 3	Sample 4	Avg	dm/dt (g/h)	Water absorbed Gel 1	Gel 2	Gel 3	Gel 4	Avg	Avg (1,3,4)	Avg (3,4)
0 (dry)	14,57	14,56	14,6	14,65	14,595		0	0	0	0	0		
0	14,75	14,67	14,74	14,77	14,7325		0	0	0	0	0		
0,083333	15,22	15,09	15,17	15,2	15,17	5,25	0,47	0,42	0,43	0,43	0,4375	0,443333	
0,166667	15,42	15,3	15,43	15,42	15,3925	2,67	0,67	0,63	0,69	0,65	0,66	0,67	

0,25	15,53	15,42	15,59	15,6	15,535	1,71		0,78	0,75	0,85	0,83	0,8025	0,82	
0,333333	15,66	15,54	15,75	15,69	15,66	1,5		0,91	0,87	1,01	0,92	0,9275	0,946667	
0,5	15,83	15,74	15,96	15,88	15,8525	1,155		1,08	1,07	1,22	1,11	1,12	1,136667	
0,75	16,04	15,91	16,17	16,1	16,055	0,81		1,29	1,24	1,43	1,33	1,3225	1,35	
1	16,24	16,02	16,36	16,24	16,215	0,64		1,49	1,35	1,62	1,47	1,4825	1,526667	
1,25	16,36	16,18	16,53	16,41	16,37	0,62		1,61	1,51	1,79	1,64	1,6375	1,68	
1,5	16,46	16,29	16,66	16,52	16,4825	0,45		1,71	1,62	1,92	1,75	1,75	1,793333	
1,75	16,55	16,35	16,7	16,61	16,5525	0,28		1,8	1,68	1,96	1,84	1,82	1,866667	
2	16,68	16,46	16,82	16,72	16,67	0,47		1,93	1,79	2,08	1,95	1,9375	1,986667	
2,5	16,82	16,62	16,96	16,86	16,815	0,29		2,07	1,95	2,22	2,09	2,0825	2,126667	
3	17,02	16,79	17,12	17,02	16,9875	0,345		2,27	2,12	2,38	2,25	2,255	2,3	
3,5	17,11	16,84	17,26	17,13	17,085	0,195		2,36	2,17	2,52	2,36	2,3525	2,413333	
4	17,22	16,91	17,36	17,22	17,1775	0,185		2,47	2,24	2,62	2,45	2,445	2,513333	
4,5	17,37	17,02	17,48	17,34	17,3025	0,25		2,62	2,35	2,74	2,57	2,57	2,643333	
5	17,47	17,11	17,57	17,43	17,395	0,185		2,72	2,44	2,83	2,66	2,6625	2,736667	
5,5	17,58	17,19	17,66	17,51	17,485	0,18		2,83	2,52	2,92	2,74	2,7525	2,83	
6	17,67	17,24	17,71	17,6	17,555	0,14		2,92	2,57	2,97	2,83	2,8225	2,906667	
6,5	17,77	17,35	17,85	17,67	17,66	0,21		3,02	2,68	3,11	2,9	2,9275	3,01	
7	17,87	17,42	17,91	17,76	17,74	0,16		3,12	2,75	3,17	2,99	3,0075	3,093333	
10	18,3	17,72	18,27	18,07	18,09	0,116667		3,55	3,05	3,53	3,3	3,3575	3,46	
21,58333	18,97	18,24	18,9	18,67	18,695	0,05223		4,22	3,57	4,16	3,9	3,9625	4,093333	
23	18,98	18,34	18,99	18,69	18,75	0,038824		4,23	3,67	4,25	3,92	4,0175	4,133333	
25	19,06	18,42	19,06	18,74	18,82	0,035		4,31	3,75	4,32	3,97	4,0875	4,2	
27	19,14	18,51	19,13	18,82	18,9	0,04		4,39	3,84	4,39	4,05	4,1675	4,276667	
29	19,23	18,61	19,2	18,95	18,9975	0,04875		4,48	3,94	4,46	4,18	4,265	4,373333	
30,5	19,27	18,68	19,24	19	19,0475	0,033333		4,52	4,01	4,5	4,23	4,315	4,416667	
46	18,26	17,68	19,57	19,33	19,45	0,025968	3+4	3,51	3,01	4,83	4,56	3,9775	4,3	4,695
48	18,18	17,67	19,64	19,43	19,535	0,0425		3,43	3	4,9	4,66	3,9975	4,33	4,78
50	-	-	19,67	19,45	19,56	0,0125				4,93	4,68			4,805
53,58333			19,8	19,57	19,685	0,034884				5,06	4,8			4,93
55,25			19,83	19,62	19,725	0,024				5,09	4,85			4,97
72,41667			19,7	19,83	19,765					4,96	5,06			5,01
74,41667				19,82							5,05			
78				19,85							5,08			
98,33333				19,85							5,08			

Stainless steel plates measured 14.18g, 14.19g, 14.22g and 14.22g respectively.

Swelling dried gelatine film at 25.5 C, made from 5 ml gel

Gravimetric experiment.

Sample 1 swollen at two days prior

Time (h)	1	2	3
0	14.46	14.53	14.68
0	14.57	14.66	14.8
0.033333	14.86	14.96	15.08
0.066667	15.02	15.13	15.23
0.1	15.13	15.24	15.34
0.133333	15.27	15.35	15.45
0.166667	15.36	15.45	15.52
0.2	15.42	15.53	15.63
0.233333	15.51	15.62	15.67

	1	2	3	Mean	SD	dW/dt	φ_w
Disc	14.17	14.23	14.32				
Film	0.29	0.30	0.36	0.316667			
Water layer	0.11	0.13	0.12	0.12	0.008165		
Imbibed	0.29	0.30	0.28	0.29	0.008165	8.7	0.53892
	0.45	0.47	0.43	0.45	0.01633	4.8	0.644594
	0.56	0.58	0.54	0.56	0.01633	3.3	0.692972
	0.70	0.69	0.65	0.68	0.021602	3.6	0.732669
	0.79	0.79	0.72	0.766667	0.032998	2.6	0.7555
	0.85	0.87	0.83	0.85	0.01633	2.5	0.774055
	0.94	0.96	0.87	0.923333	0.038586	2.2	0.788199

0.266667	15.57	15.76	15.75	1.00	1.01	0.95	0.986667	0.026247	1.9	0.799063
0.3	15.65	15.74	15.81	1.08	1.08	1.01	1.056667	0.032998	2.1	0.809843
0.333333	15.73	15.81	15.85	1.16	1.15	1.05	1.12	0.049666	1.9	0.818645
0.416667	15.83	15.90	15.97	1.26	1.24	1.17	1.223333	0.038586	1.24	0.831381
0.5	15.95	16.01	16.07	1.38	1.35	1.27	1.333333	0.046428	1.32	0.84311
0.583333	16.03	16.13	16.16	1.46	1.47	1.36	1.43	0.049666	1.16	0.852147
0.666667	16.13	16.22	16.28	1.56	1.56	1.48	1.533333	0.037712	1.24	0.860724
0.833333	16.25	16.37	16.43	1.68	1.71	1.63	1.673333	0.032998	0.84	0.870872
1	16.46	16.51	16.55	1.89	1.85	1.75	1.83	0.058878	0.94	0.880606
1.25	16.66	16.71	16.74	2.09	2.05	1.94	2.026667	0.063421	0.786667	0.890929
1.5	16.82	16.80	16.87	2.25	2.14	2.07	2.153333	0.074087	0.506667	0.896682
2	17.10	17.17	17.19	2.53	2.51	2.39	2.476667	0.061824	0.646667	0.908942
2.5	17.32	17.37	17.42	2.75	2.71	2.62	2.693333	0.054365	0.433333	0.915649
3		17.60	17.62		2.94	2.82	2.88	0.06	0.373333	0.920683
3.5		17.79	17.83		3.13	3.03	3.08	0.05	0.4	0.925449
4		18.01	18.04		3.35	3.24	3.295	0.055	0.43	0.929973
21		19.92	19.93		5.26	5.13	5.195	0.065	0.111765	0.954417
22		19.85	19.92		5.19	5.12	5.155	0.035	-0.04	0.95408
24		19.81	19.93		5.15	5.13	5.14	0.01	-0.0075	0.953952
25			19.92			5.12	5.12		-0.02	0.95378
26			19.68			4.88	4.88		-0.24	0.951617
26.5			19.54			4.74	4.74		-0.28	0.950259

Swelling dried gelatine film at 27.5 °C, made from 5 ml gel

Gravimetric experiment.

Samples 3 and 4 were swollen the day after

						1	2	3	4	Mean	SD	dW/dt	φ_w
Time (h)	1	2	3	4	Disc	14.25	14.06	14.24	13.96				
0	14.55	14.36	14.54	14.26	Film	0.30	0.30	0.30	0.30	0.3			
0	14.66	14.46	14.69	14.35	Water layer	0.11	0.10	0.15	0.09	0.1125	0.0263		
0.033333	14.99	14.77	14.97	14.66	Imbibed	0.33	0.31	0.28	0.31	0.3075	0.020616	9.225	0.56676
0.066667	15.15	14.95	15.12	14.85		0.49	0.49	0.43	0.50	0.4775	0.032016	5.1	0.67012
0.1	15.29	15.09	15.26	14.96		0.63	0.63	0.57	0.61	0.61	0.028284	3.975	0.72185
0.133333	15.41	15.21	15.36	15.07		0.75	0.75	0.67	0.72	0.7225	0.037749	3.375	0.75453
0.166667	15.55	15.35	15.45	15.16		0.89	0.89	0.76	0.81	0.8375	0.063966	3.45	0.78085
0.2	15.64	15.46	15.54	15.27		0.98	1.00	0.85	0.92	0.9375	0.067515	3	0.79954
0.233333	15.72	15.52	15.61	15.34		1.06	1.06	0.92	0.99	1.0075	0.06702	2.1	0.81083
0.266667	15.82	15.61	15.70	15.35		1.16	1.15	1.01	1.00	1.08	0.086795	2.175	0.82126
0.3	15.88	15.67	15.76	15.44		1.22	1.21	1.07	1.09	1.1475	0.078475	2.025	0.82999
0.333333	15.95	15.76	15.83	15.52		1.29	1.30	1.14	1.17	1.225	0.081854	2.325	0.83901
0.416667	16.11	15.91	15.97	15.65		1.45	1.45	1.28	1.30	1.37	0.092736	1.74	0.85355
0.5	16.22	16.06	16.08			1.56	1.60	1.39		1.516667	0.111505		0.86581
0.583333	16.35	16.19	16.21	15.86		1.69	1.73	1.52	1.51	1.6125	0.113835	1.455	0.87278
0.666667	16.48	16.30	16.29	15.95		1.82	1.84	1.60	1.60	1.715	0.133041	1.23	0.87946
0.833333	16.69	16.51	16.45	16.15		2.03	2.05	1.76	1.80	1.91	0.151217	1.17	0.89042
1	16.90	16.70	16.57	16.26		2.24	2.24	1.88	1.91	2.0675	0.199562	0.945	0.89792
1.25	17.14	16.98	16.79	16.47		2.48	2.52	2.10	2.12	2.305	0.225906	0.95	0.90746
1.5	17.35	17.22	16.97	16.69		2.69	2.76	2.28	2.34	2.5175	0.242539	0.85	0.91460
2	17.85	17.58	17.28	16.96		3.19	3.12	2.59	2.61	2.8775	0.321805	0.72	0.92448
2.5	18.19	17.98	17.47	17.19		3.53	3.52	2.78	2.84	3.1675	0.413552	0.58	0.93092
3	18.55	18.27	17.63	17.36		3.89	3.81	2.94	3.01	3.4125	0.507042	0.49	0.93556
3.25	18.52	18.26				3.86	3.80			3.83	0.042426		0.94218

3.5	18.64	18.46	17.86	17.54	3.98	4.00	3.17	3.19	3.585	0.467796	0.345	0.93847
3.75	18.74	18.50			4.08	4.04			4.06	0.028284		0.94527
4	18.73	18.58	17.9	17.69	4.07	4.12	3.21	3.34	3.685	0.47683	0.2	0.94004
20.5	19.5	19.53			4.84	5.07			4.955	0.162635	0.07697	0.95471
21.58333	19.35	19.35			4.69	4.89			4.79	0.141421	-0.15231	0.95322

Swelling of dried gelatine film at 31 °C, made from 5 ml gel

Gravimetric experiment.

Samples 3 and 4 were swollen separately

						1	2	3	4	Mean	SD	dW/dt	φ_w
Time (h)	1	2	3	4	Disc	14.28	14.33	14.27	14.35				
0	14.60	14.66	14.66	14.69	Film	0.32	0.33	0.39	0.34	0.345	0.031091		
0	14.66	14.77	14.78	14.82	Water layer	0.06	0.11	0.12	0.13	0.105	0.031091		
0.033333	15.05	15.14	15.16	15.19	Imbibed	0.39	0.37	0.38	0.37	0.3775	0.009574	11.325	0.58273
0.066667	15.27	15.37	15.42	15.46		0.61	0.6	0.64	0.64	0.6225	0.020616	7.35	0.69723
0.1	15.48	15.53	15.63	15.76		0.82	0.76	0.85	0.94	0.8425	0.075	6.6	0.75709
0.133333	15.62	15.69	15.82	15.82		0.96	0.92	1.04	1.00	0.98	0.05164	4.125	0.78380
0.166667	15.78	15.57	16.02	15.71		1.12	0.80	1.24	0.89	1.0125	0.202875	0.975	0.78928
0.2	15.80	15.75	15.95	15.78		1.14	0.98	1.17	0.96	1.0625	0.107819	1.5	0.79719
0.233333	15.83	15.85	15.95	15.71		1.17	1.08	1.17	0.89	1.0775	0.132004	0.45	0.79944
0.266667	15.84	15.89	15.90	15.84		1.18	1.12	1.12	1.02	1.11	0.066332	0.975	0.80417
0.3	15.84	15.89	15.94	15.88		1.18	1.12	1.16	1.06	1.13	0.052915	0.6	0.80696
0.333333	15.88	15.95	16.01	15.87		1.22	1.18	1.23	1.05	1.17	0.082865	1.2	0.81232
0.416667	15.89	15.96	16.09	15.96		1.23	1.19	1.31	1.14	1.2175	0.071822	0.57	0.81832
0.5	15.95	15.99	16.09	15.94		1.29	1.22	1.31	1.12	1.235	0.085829	0.21	0.82043
1	15.95	16.02	16.16	15.93		1.29	1.25	1.38	1.11	1.2575	0.112361	0.045	0.82307
2	15.50	15.63	16.06	15.55		0.84	0.86	1.28	0.73	0.9275	0.241851	-0.33	0.77433
2.75	14.39	14.99				-0.27	0.22			-0.025	0.346482	-1.27	-0.10191

Calibration of FDG, with a hydrostatic head of 90mm at 21 °C

h (mm)	time (s)	mass (g)	h/d_t	flow (g/s)
1,50	10,9	151,19	0,30	13,87064
1,40	9,75	132,27	0,28	13,56615
1,30	10,00	131,61	0,26	13,161
1,20	10,16	130,41	0,24	12,83563
1,10	10,25	126,74	0,22	12,36488
1,00	10,31	122,53	0,20	11,88458
0,90	10,09	111,76	0,18	11,07631
0,80	10,06	106,6	0,16	10,59642
0,70	10,34	102,24	0,14	9,887814
0,60	10,00	87,72	0,12	8,772
0,50	9,59	72,32	0,10	7,541189
0,45	9,90	68,29	0,09	6,89798
0,40	10,12	62,48	0,08	6,173913
0,35	10,38	57,22	0,07	5,512524
0,30	10,15	46,48	0,06	4,57931
0,25	10,22	37,16	0,05	3,636008
0,20	10,62	28,77	0,04	2,70904
0,15	10,22	18,03	0,03	1,764188
0,10	20,10	18,32	0,02	0,911443

0,05	21,09	7,7	0,01	0,365102
0,00	20,88	3,12	0	0,149425
0,05	20,66	8,38	0,01	0,405615
0,10	20,38	19,58	0,02	0,960746
0,15	10,28	18,07	0,03	1,757782
0,20	10,28	27,72	0,04	2,696498
0,25	10,37	38,24	0,05	3,68756
0,30	10,16	47,36	0,06	4,661417
0,35	9,85	51,81	0,07	5,259898
0,40	10,09	60,29	0,08	5,975223
0,45	10,00	67,82	0,09	6,782
0,50	10,1	74,75	0,10	7,40099
0,60	10,12	86,96	0,12	8,592885
0,70	10,18	97,87	0,14	9,613949
0,80	9,97	103,46	0,16	10,37713
0,90	10,40	117,49	0,18	11,29712
1,00	9,75	112,96	0,20	11,58564
1,10	10,56	127,54	0,22	12,07765
1,20	9,62	120,73	0,24	12,5499
1,30	10,16	134,16	0,26	13,20472
1,40	10,07	137,85	0,28	13,68918
1,50	10,12	135,15	0,30	13,35474