Foaming of Ethyl Hydroxyethyl Cellulose

Effects of chain length shortening

by

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Foaming of Ethyl Hydroxyethyl Celullose (EHEC)
Effects of chain length and degradation
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Abstract

The current depletion of petroleum resources together with environmental issues have led to new approaches in plastic manufacturing. This trend involves using eco-friendly materials coming from renewable resources. Good candidates for this, due to their properties and availability, are the cellulose derivatives. Some of them, such as hydroxypropyl methylcellulose (HPMC), showed in previous studies a promising behavior when making polymeric foams. Unfortunately, the corresponding results with ethyl hydroxyethyl cellulose (EHEC) were not as promising and the rather high molecular weight of the used EHEC grade was here believed to be one of the important factors, affecting the foaming ability. Therefore, in this report, the effect of chain scission and thus the chain length on the foaming behavior of EHEC was studied. The reduction in molecular weight was achieved through an addition of a degrading agent and salt to aqueous solutions of the original cellulose derivative (EHEC). After drying, the resulting polymers were characterized, both in the solid state e.g. in the form of films, and as aqueous solutions. This characterization was focused on the rheological behavior. Techniques such as rotational rheometry and dynamic mechanical thermal analysis (DMTA) were used for this purpose. The results pointed to a decrease in molecular weight when adding encreasing amounts of the degrading agent. However, the addition of salt seemed to have an opposite effect, and an increase in viscosity was observed for increasing amounts of salt. A hot-mold process and density measurements were used for assessing the foaming ability. The reduction in molecular weight allowed aqueous solutions with up to 20 and 25 % polymer content to be used in the foaming process (the optimal concentration for the original EHEC was 5 %). A higher polymer content would be beneficial with regard to large scale processing, like extrusion, one of the most common polymer processing techniques. Additionally, shrinkage was observed in some of the foams and was believed to be associated with the salt content, affecting the foaming ability negatively. Finally, the molecular weight was determined by size-exclusion chromatography (SEC). These SEC-results confirmed the reduction in molecular weight of the EHEC-grade used.

Keywords: Ethyl hydroxyethyl cellulose, cellulose derivatives, Foaming ability, DMTA, Rheological properties, Tensile tests, Shortening of chain length.

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Abbreviations

CAGR	Compound Annual Growth Rate
CD	Cellulose Derivative
DMTA	Dynamic Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
EHEC	Ethyl hydroxyethyl cellulose
EPS	Expanded Polystyrene
HPMC	Hydroxypropyl methylcellulose
LDPE	Low Density Polyethylene
LVR	Linear viscoelastic region
PLA	Poly (lactic acid)
PU	Polyurethane

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1 Introduction

Since its discovery, the consumption of plastics has grown rapidly. One reason why they are being used in many fields of industry is that together with the developed manufacturing technologies, different properties can be obtained, which makes the family of plastics truly versatile.

Even being aware of the harmful effects of fossil fuels consumption, it is difficult to change this trend due to the high economic benefits of companies in this sector. Just in the field of polymer foams, the worth of the global market in 2012 was $82.6 billion and is estimated to reach $131.1 billion by 2018, growing at a compound annual growth rate (CAGR) of 7.7% from 2013 to 2018[1]. The existing high demand from some of the biggest industries such as automotive, building and construction and packaging is continuously increasing the global polymer foam consumption [1]. Hopefully, the raised awareness about the depletion of fossil-based resources during the last decades has favored the emergence of new trends, being more respectful and considerate to nature. The use of green chemistry and engineering which tries to develop a new generation of biomaterials and products are good examples of the new trends mentioned above. Although during the following years, the consumption of petroleum will most likely continue to be very high, the renewable alternatives are the ones which will hopefully replace the conventional plastics, leading to a more sustainable production of plastics.

In the field of foams, which is the subject of this master thesis, the new trends pointing towards developing and manufacturing biofoams are in focus. Although there currently already exist several raw materials stemming from organic resources (e.g. starch, poly(lactic acid), etc), cellulose catches world's attention for being an almost inexhaustible resource of a polymeric material [2] (the most important skeletal component in plants) while combining fascinating structure and properties. Some of the first man-made plastics ever patented were made of cellulose [3] but by the emergence of fossil-based materials its use disappeared.

Cellulose is a polysaccharide built up from 1, 4-anhydroglucose (AHG) units. The cellulose molecules in native cellulose form large crystalline regions, and therefore cellulose is insoluble in water. To create water soluble cellulose-derivatives, first alkalization is needed for two purposes: to introduce charges to the molecules, making them swell and to make them available for chemical reaction while at the same time act as a catalyst for the modification reactions [4]. Some derivatives often used in industrial applications are the water-soluble cellulose derivatives [5]. Interesting candidates for production of foams originating from non-fossil resources are hydrox-

ypropyl methylcellulose (HPMC) and methyl ethyl hydroxyethylcellulose (MEHEC).

1.1 Objective/Aim

In previous studies, five samples of HPMC and four of EHEC were analyzed in order to evaluate their foaming ability [6]. The first derivative showed promising foaming properties whereas only one EHEC sample did, and even so not obtaining as good results as the HPMC. One of the factors that could be causing the different behavior is the molecular chain length.
Therefore, the main goal of this thesis is to validate or non-validate such a hypothesis. Initially, some shortening of the chain length of EHEC materials is necessary in order to reduce the molecular weight. Thereafter, observations of the influence on the chain length on the foaming behavior will be made. In this context, measurements of the polymer solutions, determination of the foam density as well as evaluations of the molecular weight of the EHEC-specimens are of importance and interest.

2 Theoretical Background

The aim of this section is to provide basic knowledge to the reader for a better representation and understanding of the results which will be subsequently discussed.

2.1 Cellulose derivatives (CDs)

The biodegradable polymers made from renewable resources have received increased attention of polymer scientists, plastics manufacturers and government agencies among others. Most of the interest in biodegradable plastics is focused at developing low cost materials that are economical in high-volume applications. Some important applications, such as packaging and consumer products, are good examples to illustrate that. Starch-based materials have been of particular interest because of its low cost [7].
As starch, poly (lactide acid) or polylactide (PLA) is a biodegradable and biocompatible polymer produced from renewable resources (cornstarch and sugarcane). It is a thermoplastic aliphatic polyester that is synthesized through a ring-opening polymerization of lactide and lactic acid monomers. During the last decade this material has been extensively studied due to its potential for replacing fossil-based polymers. Such features as being green and biodegradable, as well as the non-release of toxic components during its manufacture, endow PLA with all a material needs to become a very interesting candidate[8].
Following the same pattern, some studies are devoted to manufacturing foam from cellulose, the most abundant and widely used organic polymer in the world. After a chemical treatment cellulose can be made water-soluble. The water-soluble cellulose ethers have many applications in different areas of industry. Some of them are listed below[9].

- Water-borne paints. CDs are used as thickening and rheology modifiers. Additionally, they take an active part in the particle stabilization in the paint.
- Construction. The main objective of the cellulose derivatives in this field is to increase the water retention.
- Pharmaceutical formulations. They can be used as one component of the excipient or as a coating layer on the outside of the tablet.
- Food. Cellulose ethers are able to retain moisture evaporation, thus they are used for extending the shelf life of bread and other baked goods. They are also used as substitutes for gluten.

Although there are already many applications for CDs in general, HPMC and EHEC have a special interest due to its potentially good properties to form different kinds of foam.

2.1.1 Ethyl hydroxyethyl cellulose

EHEC is a water-soluble cellulose derivative in which both ethyl and hydroxyethyl groups are attached to the anhydroglucose units by ether linkages. Alkali, ethylene oxide and ethyl chloride are needed to manufacture EHEC from cellulose.

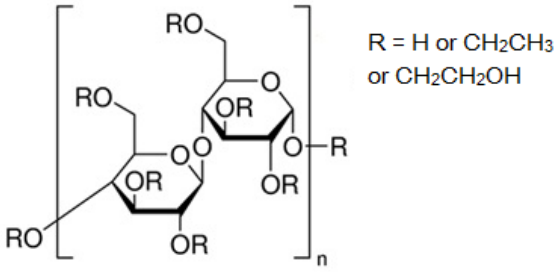


Figure 1: Schematic representation of the chemical structure of EHEC. Figure adapted from [6]

Although EHEC already has other applications in fields such as painting, this study will be focused on the manufacturing of foams from this material.

2.2 Foam characterization

Attributes related to the molecular structure of polymers can make them more or less successful for processing. Unlike metals or ceramics, polymeric materials often consist of very long chain-like macromolecules. For this reason, it is important to know the different material properties defining the polymeric material before studying it.

2.2.1 Glass transition temperature (T_g)

One of the fundamental parameters describing polymers is the glass transition temperature, T_g. The material behaves in an increasingly brittle manner if the temperature drops below T_g whereas its behavior is more rubber-like above this temperature. Materials which are formed by long chains, networks of linked atoms, or those having a complex molecular structure are the ones exhibiting a glass structure. When such materials (which usually have a high viscosity) undergo a rapid cooling from above T_g to a temperature below that, the structure cannot reorganize itself into a crystalline structure. During this cooling the molecular movement is too sluggish, or the molecular structure too awkward, to take up a crystalline conformation.

Consequently, the random arrangement distinctive of the liquid persists down to temperatures where the viscosity is so high that the material is considered to be solid. The term glassy is recognized as a permanent non-equilibrium state and in some cases even a way to achieve a state of lowest energy might not be available. Despite this scientific significance of glass forming-materials, the glass transition itself is poorly understood. In particular, it is not clear whether the glass transition is a thermodynamic transition [11] or a purely kinetic phenomenon [12].

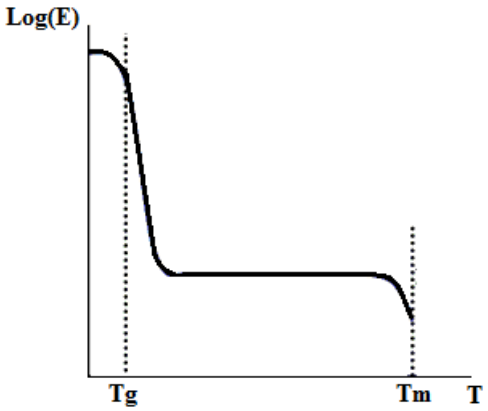


Figure 2: The temperature dependence of the tensile modulus E. The glass transition temperature T_g as well as the melting temperature T_m are indicated.

As can be seen in figure 2, there are three regions clearly differentiated. Bellow T_g, there is a temperature range where the material exhibits a more or less constant value of the tensile modulus E, followed by a decrease of E when T_g is approached. Once this temperature is exceeded a second plateau is reached and the last region corresponds to the melting temperature (if the polymer is semi-crystalline).
Using dynamic mechanical thermal anylisis (DMTA) technique (which will be explained in more detail in the next sections), T_g can be found. T_g is determined by the large drop in the chart log(E')/Temp (at the same time, in the tan(δ) curve, a peak can be seen).

2.2.2 Storage and loss modulus

When a sinusoidal strain is applied to the sample, two components are defining the corresponding stress. These components represent the elastic part of the response (also called storage modulus and represented by E' when a tensile strain is applied or G' for shear strain) and, on the other hand, the viscous part (or loss modulus, represented by E" or G" depending on the kind of strain applied). The value of these parameters depend on the phase δ (phase shift between the stress and the strain on the sample). For an ideal elastic material δ=0° (energy stored) and δ=90° for a liquid viscous material (energy dissipated). The usual way to represent them

is from a right-angle triangle, having tanδ as a quantifier of the balance between energy loss and stored energy. Therefore, if the material is more viscous the value of tanδ is greater than 1 and lower when the material has a more solid behavior.

The parameter tanδ can also be understood as the phase difference between the stress and the strain applied. The ratio *E"/E'* or *G"/G'* (which is tanδ), is also a quantifier of the internal friction of the material.

2.2.3 Viscosity

In short, the viscosity quantifies fluids resistance to flow. It is represented by the symbol "eta" and it is calculated as the ratio between the shear stress and the velocity gradient.

$$\eta = \left(\frac{F}{A}\right) \div \left(\frac{\partial v}{\partial y}\right) \tag{2.1}$$

Although the equation shown above is the general expression, the viscosity is normally represented by Newton's equation. This equation states that the resulting shear ratee in a fluid is directly proportional to the force applied and inversely proportional to its viscosity.

$$\left(\frac{f}{A}\right) = \eta \left(\frac{\partial v}{\partial y}\right) \tag{2.2}$$

The unit used by the International System of Units to define viscosity is the pascal second [Pa s]. Nevertheless, another common unit is the dyne second per square centimeter also known as Poise referring to the French physiologist Jean Poiseuille (1799-1869). Since ten Poise equal one Pa $\cdot$ s, the conversion of units is straightforward.

What has been discussed up to now is also known as the dynamic viscosity. Another expression for viscosity is sometimes used. It is called kinematic viscosity and it is the ratio between viscosity of a fluid and its density:

$$\nu = \frac{\eta}{\rho} \tag{2.3}$$

Viscosity describes the resistance to flow at a particular temperature. A high or low internal resistance to flow will define high and low viscosities respectively. Normally, longer chain molecules lead to higher viscosity (such as plastics). As a general rule for polymers, the viscosity decreases when increasing the temperature (the opposite happens with gases).

When measuring the viscosity, it is usual to represent it in a chart log(η)/shear rate. It is easy to distinguish two basic parts in the characteristic curve for polymers:

first a plateau at low shear rates and, after a threshold value of the shear rate, the viscosity decreases.

2.2.4 Viscoelasticity

The classical theory of elasticity considers mechanical properties of elastic solids following Hooke's law. The deformation is proportional to the applied strain. On the other hand, the hydrodynamic theory understands the properties of viscous liquids according to Newton's law, that is, the resulting strain rate is proportional to the applied stress. Both are idealized models, many solids follow Hooke's law when the deformation is small and many liquids follow Newton's law when the deformation rate is low. Viscoelastic materials combine both behaviors, thus the strain can partly recover when the stress is released.
For Newtonian fluids, viscosity η is a material constant and not dependent of the rate of deformation. For elastic materials the strain is directly proportional to the stress with a proportional factor called shear modulus G (for shear) or Young's modulus E (for tension), and the elastic energy is stored in the substance when deforming it. The strain is totally recoverable after the load is removed, provided that the limit for onset of plastic deformation was not exceeded. For purely viscous materials all the energy is dissipated in the form of heat, thus the recoverable strain is zero [13]. Polymeric materials are in general non-Newtonian since they consist of long molecules that entangle with each other, creating flexible and reversible "joints". The polymeric behavior is Hookean and Newtonian, making polymers viscoelastic materials. Moreover, to have a more straightforward characterization of the materials it is convenient to test them in the linear viscoelastic region (LVR) where the viscoelastic properties are independent of applied stress or strain levels.
Due to the complex behavior of viscoelastic materials and in order to study the flow properties of foams, rheology will be used. This science, from the Greek reos (flow) and logos (study) as well as defined by Heraclitus as panta rei (all things flow), is useful to describe such properties.

2.2.5 Cloud point

Cloud point measurements is a common method to determine phase boundaries and phase separation [14]. At temperatures above the cloud point the polymer is no longer completely soluble in the fluid, giving a cloudy appearance.
In order to obtain good mixtures, i.e. a polymer solution, the temperature during the mixing process should be above the cloud point. One way to ensure that the mixing takes place above a certain temperature could be by adding some extra chemical (e.g. NaCl, Na_2SO_4, $CaCl_2$, etc.) as has previously been done with some non-ionic surfactants [15][16]. At the same time, one has to be careful and ensure

that the chemicals added are not negatively affecting the reaction since it could affect the expected outcome.

2.2.6 Size-exclusion chromatography(SEC)

The concept of separation by size using chromatography was first discussed by Synge and Tiselius [18]. They observed that small molecules could be excluded from the small pores of zeolites depending on their molecular size [19]. The first examples of SEC were introduced by Wheaton and Bauman [20] in their work on ion-exclusion chromatography.
Chromatographic techniques separate molecules by taking advantage of the distribution of the different components between two parts: the steady phase and the mobile phase.
SEC is a liquid type of chromatography where the steady part is solid and the mobile is liquid. This technique is also called Gel Permeation Chromatography (GPC). Its principal application is molecule separation according to the size in order to study the molecular weight and the polymer distribution.
The material which fills the column is acting as a sieve and different molecules can be distinguished by size [21]:

- Permeable molecules: small molecules which go slowly through the porous phase since they are withheld in the pores.
- Divisible molecules: molecules which enter partially in the pores.
- Excluded molecules: the molecules bigger than the pores which can go through the column faster than the smaller ones.

The sieve, which represents the steady phase, is made by a porous material and varies depending on many variables such as pore's size, temperature, accuracy, range of molecular weight, etc. The pore size, together with the geometry, restricts access of molecules based on their Stokes' radius. Consequently, the largest polymers, which are excluded from the pores, leave the column first, that is, polymer elute in order of decreasing size. But there are also other factors which affect the measurements such as shape or molecule linearity. Nevertheless, this technique allows the use of calibrated curves, derived from a set of known analytes, to be used to estimate the molecular weight of an unknown analyte. Typical calibration curves are based on polymers of known molecular weights. The mobile phase (fluid) has to drag the dissolved polymers without reacting neither with it nor with the steady phase.
At the end of the column is a device which calculates some features of the particles leaving the system. Light scattering sensors and refraction index measurements are examples of such devices. Below, a schematic figure of a whole system can be seen.

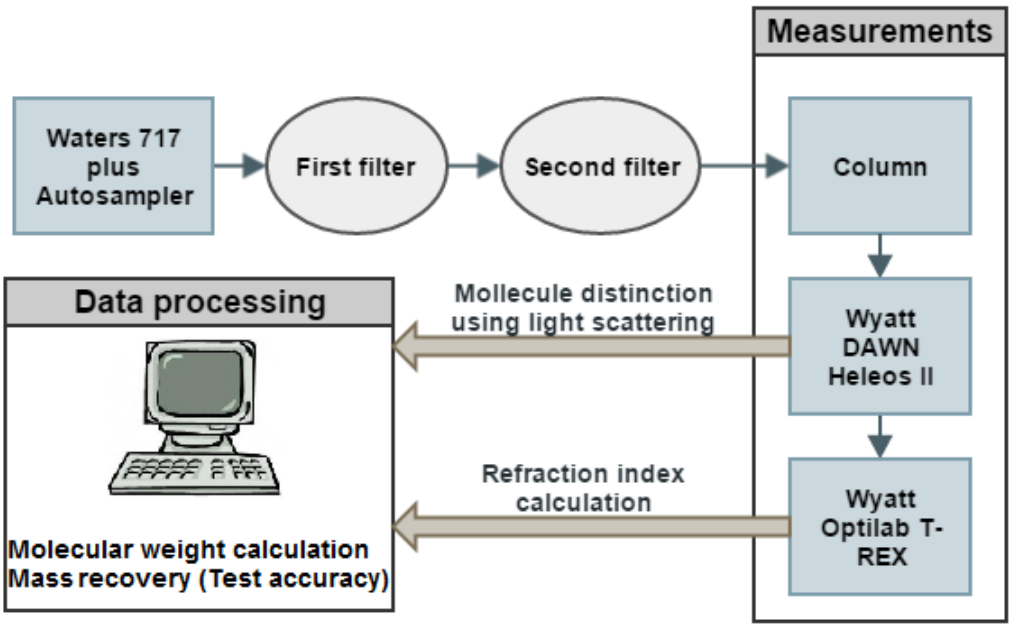


Figure 3: Schematic representation of a system used for SEC.

Due to the range of chain lengths that is at hand in a polymer, its molecular weight can not be defined with a single value. Therefore, the molecular weight of a polymer must be described using an average taking into account all the different chain lengths of the sample. The most common measures of the average molecular weights are M_n (number average) and M_w (weight average) and their definitions are:

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \qquad\qquad M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{2.4}$$

The ratio between M_w and M_n is called polydispersity index. It is used as a measure of the broadness of molecular weight distribution of a polymer.

2.3 Hot-mold foaming

Although there are many foaming techniques such as baking, freeze-casting or by extrusion among others, just the first one, which is also called compression molding, will be used during this master thesis. This technique has been intensively investigated for processing starch-based polymers, particularly foamed containers [22]. Therefore it was considered a good option when testing the foaming ability of the cellulose derivatives. Not only is it an easy way to foam the different samples but also a relatively fast technique.
The process principally consists of applying pressure on the sample, which is poured

in a preform or mold, by means of two plates that can be heated individually. Normally, the test material needs to be mixed with an external blowing agent which creates the foam when it is activated either due to temperature, pressure or both. For example, when water is the blowing agent, due to its evaporation over 100 °C the bubbles created give the foam structure.

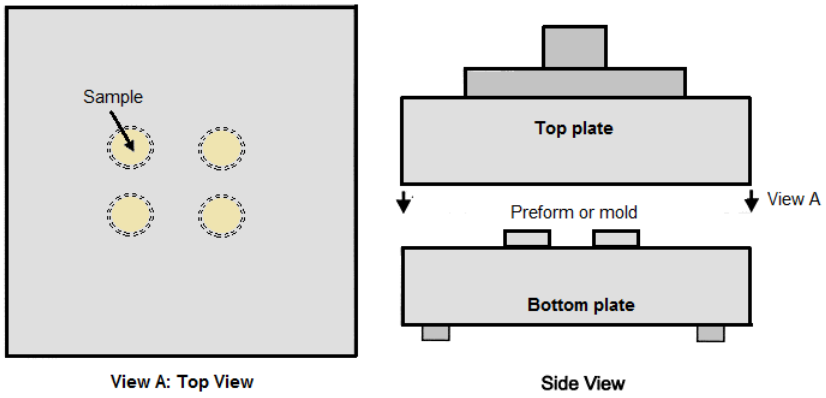


Figure 4: Schematic picture of hot-mold foaming.

2.4 Rheology

Rheology is the science of flow and deformation of materials. A strain or strain rate creates a deformation and indicates the distance that a certain material element moves under the influence of an external force, or stress. As has been mentioned before, the behavior of materials under stress or strain varies from purely viscous to pure elastic (or a combination of both, viscoelastic materials). This behavior is reflected in measurable properties such as modulus, viscosity and elasticity.
Many materials present a complex rheological behavior. Material processability as well as end-use performance are determined by the rheological properties. This shows how important rheological measurements are for the whole range of different materials including ceramics, petroleum products, elastomers, pharmaceuticals, etc [23].
Rotational rheometers as well as DMTA instruments are commonly used equipment for evaluating the rheological properties and will be described further in the next sections.

2.4.1 Rotational rheometer

Most commercial rheometers measure the viscoelastic properties using a rotational geometry. There are three very common geometry set-ups, although the most used are the parallel plates and the cone-plate. These two set-ups, together with the one with concentric cylinders, are shown in Figure 5. The experimental procedure to

obtain the results is similar in all cases. Depending on the type of material being evaluated, one or the other set-up should be used: concentric cylinders for very low to medium viscosity, cone-plate for very low to high viscosity and plate-plate for low viscosity to soft solids.
Moreover, most commercial rheometers use a mode called simple shear deformation. In this mode, one surface is fixed whereas the other is rotated (either with a strain or a given strain rate). The result obtained from the rheometer can be a shear stress if the strain is being controlled or the strain if the shear stress is being controlled.

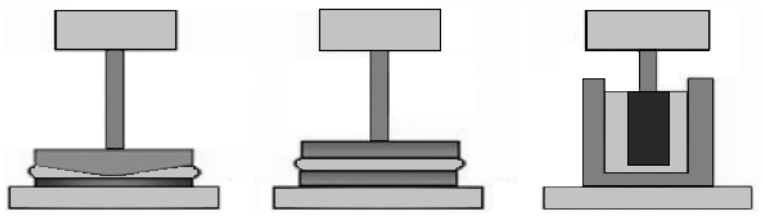


Figure 5: From left to right: A schematic display of the rheometer gap fixtures; cone-plate, plate-plate and concentric cylinders.

2.4.2 Dynamic Mechanical Thermal Anlysis (DMTA)

The first attempts to do oscillatory experiments to characterize the elasticity of a material was made by Poynting in 1909 [25]. The utilization of oscillatory experiments is today a basic procedure to measure properties of polymers, such as viscosity or storage and loss moduli and at the same time taking into account the influence of temperature.
Rheology, has a reputation of being difficult to understand, involving a fair degree of mathematical sophistication [26]. Nevertheless, dynamic mechanical thermal analysis is more straightforward. For this reason, it is widely used to characterize material properties as a function of different variables such as temperature, frequency, stress or a combination of them. During the test, a small deformation is applied to the sample, with a known geometry, being studied. Either controlled stress or strain can be applied on the subjected sample. The stress applied in a DMTA is sinusoidal and depending on the stiffness the sample will deform a certain amount. One of the concerns has always been the stabilizing bearing of the shaft due to the fact that it is activated by a force motor and it is not always easy to hold it in position.
This technique allows to measure parameters such as modulus, $\tan(\delta)$ and glass transition temperature and it is also helpful to find the LVR (linear viscoelastic region). These parameters change with temperature and transitions in the sample can be seen due to the temperature control. The stress applied is sinusoidal, thus, the modulus can be expressed by the storage and loss components.

3 Materials

In this section, a short description of the materials used in the experiments is given. The main goal is to give few relevant details and some specific information about each material being used.

3.1 Water

The concentration of ions in tap water could change from one day to the other. Therefore, deionized water was used in all the experiments. This precautionary measures were taken to avoid a negative alteration of the results since the ions could possibly have some influence on the material properties. Additionally, if the results need to be compared with others, such comparison will be more relevant since the experiments were carried out from the same basis.
As exception, mili-Q water (higher purity than the deionized water) was used for the SEC measurements.

3.2 Sodium sulfate (Na_2SO_4)

Sodium sulfate was kindly provided by Akzo Nobel Product and Process Chemistry - Performance Additives. This chemical was used to reduce the cloud point and facilitate both mixing and filtering procedures.

3.3 EHEC

The ethyl hydroxyethyl cellulose used came from Akzo Nobel. It is the focus of this work. Different types of this cellulose derivative can be found on the market, the one used here was a grade denoted M10. More details are given in Table 1.

Table 1: Details of M10 composition. DS-degree of substitution, the number of hydroxyl groups per 1,4-anhydroglucose unit that have reacted. MS-molecular substitution, the average total number of ethylene oxide groups per 1,4- anhydroglucose unit. HM-hydrophobically modified, M-methyl.

Name	Viscosity (mPa s)	DS-ethyl	DS-methyl	MS-ethylene oxide
M10	750-1000	0.2-0.3	0.7-1.3	0.3-1.2

3.4 Sodium hypochlorite (NaClO)

The agent used to shorten the chain length of the EHEC used was sodium hypochlorite. This product, just like the last two, was kindly supplied by AkzoNobel. Additionally, it is considered a very corrosive product and the contact with the skin and eyes must be avoided.

4 Experimental procedure

The main goal of this study is to determine how a shortening of the chain length of EHEC affects the material properties and evaluate if said shortening has any positive influence on the foaming ability of the material. To do so, the following experiments and measurements were carried out.

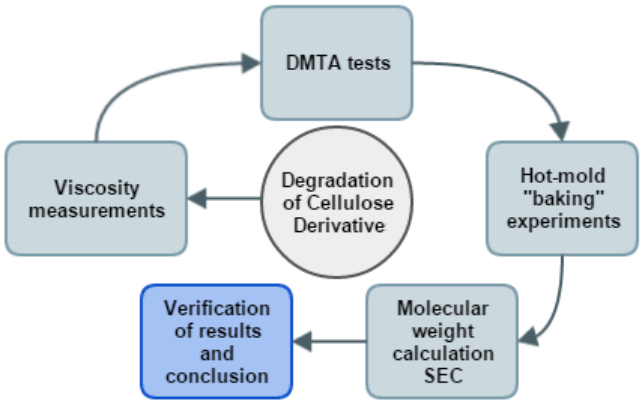


Figure 6: Schematic picture showing the different steps followed during the experiments.

As can be seen in the schematic, several devices are involved. Care should be taken during all the experiments so that reliable data can be obtained. A properly calibrated instrument, a properly prepared samples, using the right geometry, applying both reasonable strains and heating rates can be good examples of precautionary measures.

4.1 Chain shortening of cellulose derivatives

The following experiments were carried out at AkzoNobel laboratories in Stenungsund (Sweden) in order to reduce the molecular weight of the cellulose derivative EHEC. In order to achieve this, the shortening of cellulose ether chains was needed. Hereafter, a list of the equipment as well as the chemicals used is given.

- **Equipment**: Heater, Kettle, Buchner funnel, Filter paper, Holders with tube clamps, Lab jack, Control temperature device (control unit + thermometer), Pipette, Spoons, Beakers, Lab coat, Security gloves, Security glasses, Digital scale, Propeller (mixer), Reaction vessel with flat flange, Cork ring, Evaporating dish, Oven, Aluminum foil, Grinder.

- **Chemicals**: Deionized water, sodium sulfate (Na_2SO_4), EHEC M10, sodium hypochlorite (NaClO).

Once the setup of the equipment was completed, the chemicals were prepared and all the security measures were taken into account, the experiment could start. Figure 7 illustrates a possible set-up for the experiments. Although it is not shown in the photo, it is advisable that a balance is close to the rest of the equipment and in the same fume hood so that possible spill can be avoided. It is particularly a problem for the NaClO since its corrosive nature could be dangerous.
After everything was ready, water was boiled with the kettle and it was poured in the reaction vessel. The heater, the control temperature device and the propeller (mixer) were switched on. The temperature had to be adjusted a few degrees above 90°C to avoid too much water evaporation (the temperature had been set up to 93°C) and aluminum foil was used to avoid heating losses. Next, the different amounts of chemicals were measured, thus, beakers, spoons or pipettes and the balance were used. The order in which the different products were added made a difference. First, the sodium sulfate was added and dissolved in the water. After the addition, the required temperature cited before should be reached and then the M10 was added. Following the same procedure, sodium hypochlorite was added little by little just to ensure that everything went as expected (it was the only chemical with corrosive properties and therefor considered dangerous).
After 30 minutes (this time had been chosen taking into account that in previous studies, after 15 minutes, no substantial changes in the molecular weight were detected), the slurry was filtered in a funnel with the paper filter and the aspiration circuit switched on. It was necessary to check that the filtering flask was hermetically connected with the funnel as well as with the aspiration circuit to ensure a good performance during the filtering. Depending on the concentration of NaClO and salt added, the time that the slurry should be filtered differed (low amounts resulted in longer filtering times since the cloud point was not reduced and hence lower shortening of the chain length was expected). If the time spent was bellow a threshold, the product remained too wet and after drying it in the oven the resulting product was difficult to obtain in powder form.
Once the filtration was finished, the remaining product of the funnel was poured in an evaporating dish. The largest parts were grinded in order to facilitate water evaporation when put it in the oven. The oven temperature was set to 60 °C and, in order to obtain an inert atmosphere, it was filled with nitrogen gas and vacuum was applied.
In order to determine which experimental parameters were of more interest, an experiment from a similar procedure carried out using another cellulose ether was

studied. In that experiment the different amounts of chemicals were adapted to another cellulose derivative and after observing the results obtained the steps for the EHEC were decided. For instance, after realizing that the cloud point was lower than initially thought, the amount of salt added in further experiments was reduced.

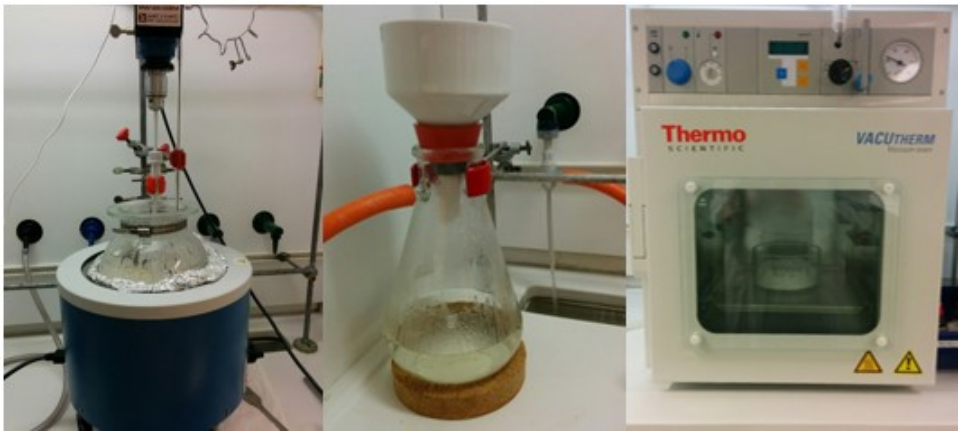


Figure 7: Part of the needed set-up to proceed with the experiments. From left to right: heating vessel where the mixing took place, filter flask and oven.

4.2 Viscosity measurements using TA instruments AR-G2

Viscosity measurements were carried out for three main reasons. First, in order to compare the change in viscosity of the degraded samples to the M10 reference sample. Secondly, the measured viscosities served as a basis for determining further experiments (higher or lower amount of sodium hypochlorite). Finally, viscosity is one of the most important characteristics of polymer solutions and thus an important property.

All the different powders obtained during the chain shortening were mixed with deionized water in order to obtain 2 % polymer solutions. A controlled stress rotational rheometer ARG2 from TA Instruments Ltd, with a cone-plate setup was used to measure the viscosities. Additionally, the measurements were repeated with the powders with higher amounts of NaClO using 5 % solutions.

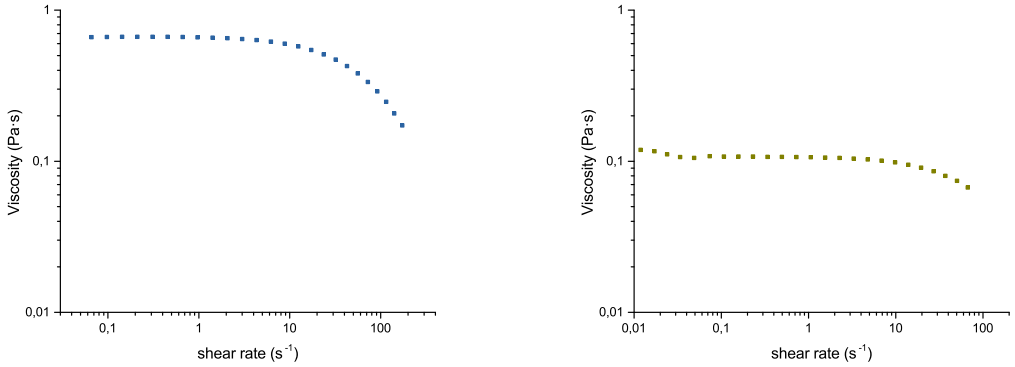


Figure 8: Example of two viscosity charts obtained using a rotational rheometer ARG2 from TA Instruments Ltd.

Moreover, to ensure a better accuracy of the results, each measurement was repeated twice and four times if the results were ambiguous. Apart from the better accuracy, they were repeated to see if any drastic change in viscosity took place over time. Fortunately, the variable time did not show a negative effect on the measurements.

4.3 DMTA measurements using RSA II

Three different experiments were carried out with Rheometrics Scientific RSA II. Each one of them had a different objective. The first one was used to establish the Linear Viscoelastic Region (LVR). The second one was to determine the glass transition temperature. The last set of experiments was a baking simulation to observe the evolution of the foam phases with temperature.
For the first two tests, films are required and, for the third one, solutions. The recommendations for the film dimensions were defined as follow (according to the manual of the instrument): 35 mm length, width up to 12.7 mm (6 mm optimal) and thickness up to 1.5 mm and not thinner than 0.01 mm. Due to the use of a Petri dish to obtain the film, it was easy to fulfill the first two dimensions and for the thickness a simple calculation as shown in equation 4.1 was necessary. Initially, a 0.1 mm thickness was chosen.

$$dry\ film\ thickness = \frac{wet\ film\ thickness\ x\ polymer\ content(\%)}{100} \tag{4.1}$$

For the solutions, deionized water was heated to 90°C before the powder was added. A higher temperature favors the mixing. Once the solution was homogeneous it was let to cool down before being used.

4.3.1 Linear Viscoelastic Region (LVR)

In order to find LVR, a strain sweep was applied as part of a tensile test. The different samples (films with the according dimensions) were placed in the clamps and the tensile test could start. Once the test was finished, a chart representing storage and loss moduli and tanδ as a function of the strain applied, was obtained. Apart from being an important parameter to define the material behavior it was also measured due to the fact that it was needed for the temperature sweep.
Another fact that needs to be taken into consideration when measuring LVR is the static force since a tensile test is performed. It is necessary to maintain a value greater than the lowest force level reached in the dynamic oscillation, if not, buckling will occur and part of the stress signal is truncated and data quality is negatively affected.

4.3.2 Glass transition temperature (T_g)

In order to determine an approximate value of the T_g and study the temperature dependence of the viscoelastic behavior of the different samples in a dry state, a ramp temperature test was carried out (oscillatory measurements at a frequency of 1Hz, heating rate from 5 to 7 °C/min and using a stable value of the strain(%) from the LVR obtained in previous tests). The films were placed in the clamps in the same way as before and the output was a chart representing the temperature dependence of the storage and loss moduli and tanδ. A first approach to find the glass transition temperature was through the definition - T_g is the temperature at which the log(E') - temperature curve starts to decrease substantially. This was done by drawing two lines in the log(E') curve, one from the beginning of the flat part and the other one following the slope where the substantial decrement takes place. The approximation of T_g can be found drawing a vertical line from their intersection.

4.3.3 Baking simulation

The configuration with two parallel heated plates was used for the baking simulation. It allowed the study of different phases as the solution was heated and also the evolution of the changes in stiffness while the temperature increased. Apart from the normal simulations where the oven was closed during all the time, some tests were repeated opening the oven every 20 °C in order to take a photo and follow the course of events visually.

4.4 Foaming with hot-mold machine

As has been noted earlier, this is a uncomplicated technique which is, taking into account previous studies, suitable for foaming. During the experiments, the concentration of polymer was changed from 5 to 25% depending on the amount of NaClO used and the viscosity. First, 10% solutions were used and depending on the results, the amount of polymer was decided. Here, water was use, both as plasticizer and blowing agent. The mixture was poured on one of the plates, filling the preform made of aluminum foil (circular profile with a diameter between 25 and 30 mm). The hot-press machine used for baking was a Franz Haas Waffelmaschinen together with a temperature control system (Figure 9).
The temperature of the plates was varied from 140 to 220 °C and the molding times from 8 to 15 minutes. No additional pressure, except for the plate's weight, was applied, thus, the external agent was activated due to the elevated temperature (above water evaporation temperature) and time.

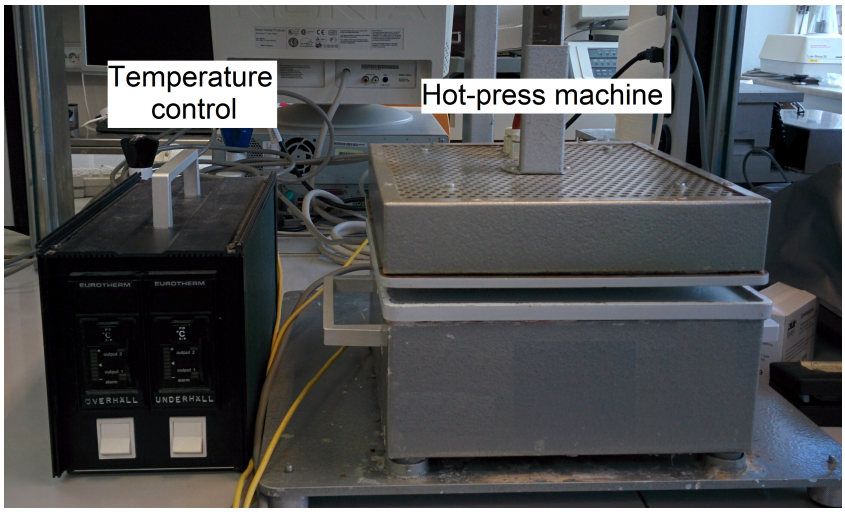


Figure 9: Press-hot machine used for the "baking" experiments.

4.5 Size-Exclusion Chromatography (SEC)

These experiments were carried out at the Department of Chemistry and Chemical Engineering, Chalmers. The different solutions made by mixing miliQ water and the cellulose derivatives with shortened molecules were poured into plastic vials. The set of samples was placed in a Waters 717 Plus Autosampler, where the experiments were performed. Sample is taken from each vial and, after being filtered twice, arrives at the column. Next, the size of the particles are analyzed by the unit Wyatt DAWN Heleos II and Optilab T-REX. All the data gathered by the last unit is sent to the computer system where data processing takes place, and the results are

obtained, i.e. the molecular weight distribution.

4.6 Density

In order to determine the density of the produced foams two different methods can be considered. Depending on the shape of the resulting foam, one method or the other will be appropriate. The solutions are placed in cylindrical preforms made of aluminum foil inside a "baking" machine in order to obtain cylindrical shape. It permits a further comparison between different samples since the same procedure is followed in all cases.

If the foam has filled the preform and completely adapted the cylindrical shape it is easy to determine the volume and hence the density (it is just necessary to weigh it). This method is faster but the approximations made when measuring the dimensions can drastically affect the accuracy of the result.

If the formed foam is far from the mold shape the density can be measured using a sand displacement method. It consists of measuring the volume when the sample is immersed in a measuring cylinder full of sand. Dividing the weight by the volume, the density is obtained. Although it is a longer procedure, it might be more accurate than the previous one since geometrical shapes can be difficult to measure with sufficient accuracy.

5 Results and discussion

In this section, all the results obtained from the experiments will be shown and discussed.

5.1 Chain shortening of cellulose derivatives

The amounts of chemicals used for lowering of the molecular weight of EHEC are given in the following table.

Table 2: Summary of chemicals used in each experiment.

Experiment	**Na_2SO_4(g)**	**NaClO(g)**	**%wt(NaClO)**
1	100	15	2
2	50	30	4
3	0	30	4
4	20	60	8
5	20	7.5	1
6	20	15	2
7	20	0	0
8	0	7.5	1
9	20	30	4
10	20	0	0
11	0	7.5	1
12	20	3.75	0.5
13	20	15	2

Some of the amounts were fixed for the whole set of experiments, for example 1000 g of water and 100 g of M10. The main reason why these amounts were fixed is because the study was focused on how the molecular weight of M10 was reduced and sodium hypochlorite had the greatest effect in this respect and therefore the one that should be changed. Following a similar approach, the temperature was set to 93°C and 30 minutes of duration for each experiment. Fixing these four variables the number of experiments were limited, making it easier to evaluate the effect of the variable parameters.

Addition of sodium sulfate reduce the cloud point of the MEHEC and is used to simplify the stirring and mixing in the reactor and the filtration after the reaction. To find the optimal amount of sodium sulfate required to give both good mixing and filtering, the first four experiments were focused on optimizing this amount. Both 100 g and 50 g resulted in easy mixing and filtering. In contrast, some problems were

detected especially with filtering when no sodium sulfate was added. Addition of 20 g sodium sulfate resulted in good mixing and acceptable filtering and was selected as the optimal addition.
After the amount of sodium sulfate had been determined, the only remaining degree of freedom was the amount of sodium hypochlorite. To determine how much of this chemical was needed, the experiments were combined with viscosity measurements (the corresponding results and discussion will be given in the next subsection). It was decided that five different amounts of sodium hypochlorite would be added: 0.5, 1, 2, 4 and 8 weight-% (%wt) (plus one reference experiment without addition of sodium hypochlorite).
As can also be seen in the table 2, three experiments were repeated. Number seven and eight had either low content of salt or degrading agent and the first time they were carried out, the filtering time was not adequate. As a result, after they were dried in the oven, the product obtained did not meet the expectations of being separable into a powder form again. Nevertheless, the second time (experiment number 10) a powder suitable for further tests was obtained. Experiment number six was done twice to evaluate the repeatability.
The quality of the powder (how easily it could be obtained again after the procedure and how fine it was) also deserves a comment since many properties are evaluated from solutions and a finer powder means better mixing and hence quality of the solutions. The main findings from the experiment was that the more salt that was added, the easier it was to obtain the final product in the form of a fine powder. Consequently, number one and two showed the best performance in this respect and the rest of the samples exhibited similar performance.

5.2 Viscosity measurements

Viscosity tests were carried out using 2 % solutions and the values, which were obtained at a shear stress of 1 Pa, are given in table 3.
For the experiments with higher contents of sodium hypochlorite, the tests were repeated with 5% solutions but the results did not differ from the first trials. In general, when the level of sodium hypochlorite was increased, the viscosity decreased. As can be seen in figure 10(a), for low contents of sodium hypochlorite, the reduction is not very pronounced whereas for 2 % and 4 % the change in viscosity was more drastic. Between 4 and 8 % only a small change can be observed.

Table 3: Viscosities of the polymer solutions for the different experiments including the original M10. The polymer concentration was 2 $\cdot$ %wt.

Experiment	**Viscosity (mPa $\cdot$ s)**	**Experiment**	**Viscosity (mPa $\cdot$ s)**
1	98	8	-
2	22	9	10
3	7	10	763
4	7	11	107
5	536	12	671
6	52	13	62
7	-	M10	19720

A similar trend was also observed in case of the amount of salt added. The measurements revealed that, although it favored the mixing process and a better powder was obtained, the amount of salt added affected the chain-length shortening negatively giving a higher molecular weight. Therefore, higher viscosities were obtained for the same percentages of NaClO (shown in Figure 10(b) where, for the same amount of sodium hypochlorite, 4%, the amounts of sodium sulfate were changed to 0, 20 and 50 g).

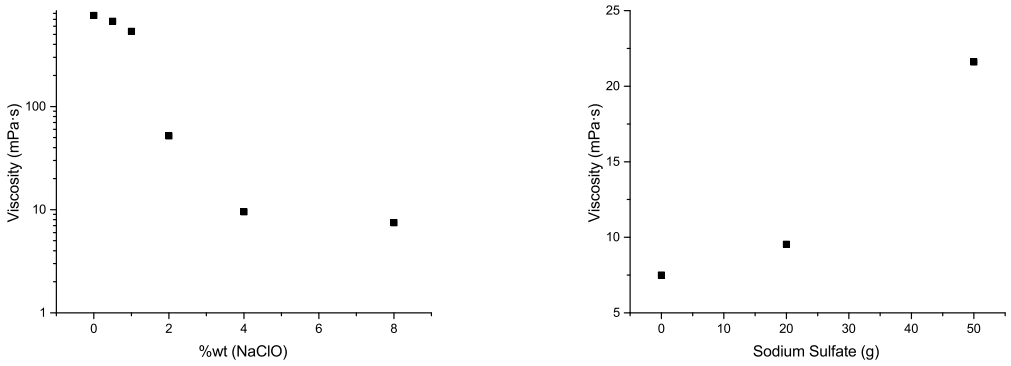


Figure 10: Left(a): Viscosity at different levels of sodium hypochlorite (20g of sodium sulfate). Right(b): Viscosity at different levels of sodium sulfate (at 4 %wt sodium hypochlorite).

Considering the effect of the salt on the viscosity, it was considered appropriate to support the result with the original M10. Consequently, 20 g of salt was added to the M10. The viscosity was expected to be slightly lower than the reference. A small lowering of the viscosity could be expected due to the sample being exposed to an elevated temperature for 30 minutes. Possibly, some interaction with the salt could also result in a lowered viscosity. However, the result was that the viscosity

was clearly below that of the original M10, see figure 10(a). Further studies are needed in order to find an explanation to this phenomena.
Further discussion is needed for the similar results obtained for experiments three and four; figure 10(b). One explanation for this similarity could be the accuracy of the machine but this option was dismissed. The second hypothesis, the more likely one, was to assume that there exists a certain limit of sodium hypochlorite after which no lower molecular weight is achieved. To verify such a hypothesis, further studies in the matter are needed.

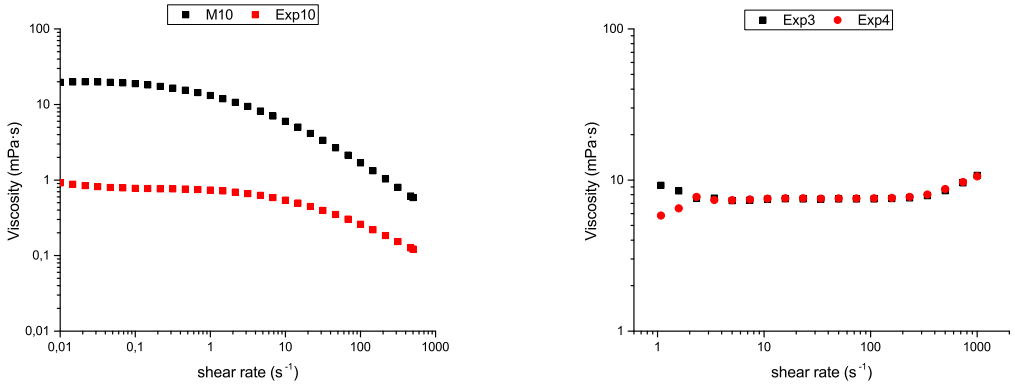


Figure 11: Left(a): Original M10 with and without salt (Exp10). Right(b): The same for experiments 3 and 4.

For experiments three and four, it was observed that the values of viscosity tended to exhibit a slight shear-thickening behavior at higher shear rates. However, that behavior is believed to be an artifact due to the low viscosity and high shear rates, the results under such circumstances could therefore not be trusted.

5.3 DMTA measurements

5.3.1 Linear Viscoelastic Region (LVR) and glass transition temperature (T_g)

As Table 4 shows, the T_g didn't vary significantly between the specimens from the experiments listed in Table 1. Thus, changes in molecular weight did not drastically affect the softening temperature. Moreover, the values measured (between 170 and 180 °C) for the glass transition temperature was comparable with values reported for similar cellulose derivatives [27].

Table 4: Glass transition temperatures (Tg) of the different specimens from experiments and the original M10.

Experiment	Tg (°C)
1	175
2	176
3	176
4	172
5	174
6	179
9	168
10	178
12	177
13	179
M10	175

5.3.2 Baking simulation

As has been discussed earlier, baking with the hot-press machine is a fast way to evaluate the foaming ability. However, in order to evaluate the different transitions occurring during the heating, a simulation using the DMTA machine is a good option. The oven was opened every 20 °C and a photo was taken. The result is shown in Figure 12. During the first 40 °C an emergence of blurry bubbles inside the solution was observed. Around 100 °C (evaporation temperature of water), there was a transition from a transparent to an opaque appearance (white color shade) and the foam formation took place. Then, from 120 to 160 °C the foam stabilizes. Finally, different stages of degradation took place (the higher temperature, the more degradation).

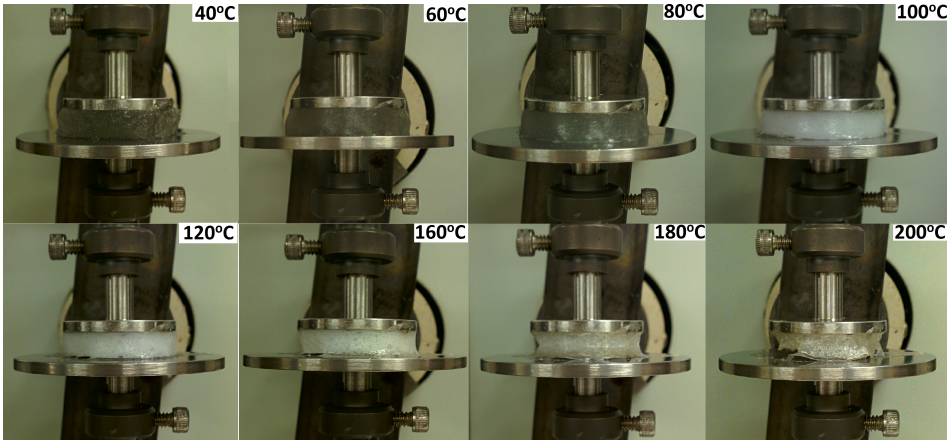


Figure 12: Baking simulation in the DMTA equipment using experiment number 4.

Except for the visual evaluation, a more detailed study was carried out by analyzing the evolution of stiffness of the sample (corresponding to E' in Figure 13). Due to the increase of temperature a growth in stiffness could be seen. Around 100 °C, when the water is evaporating, the stiffness was reduced somewhat, but after 120 °C it increased again. Above about 170 °C, a reduction of the storage modulus took place, probably due to degradation of the sample. Even though, the results obtained could be connected with foam formation and it should be pointed out that the experiment was considered as a simulation and could not be directly linked to the hot-mold baking experiments.

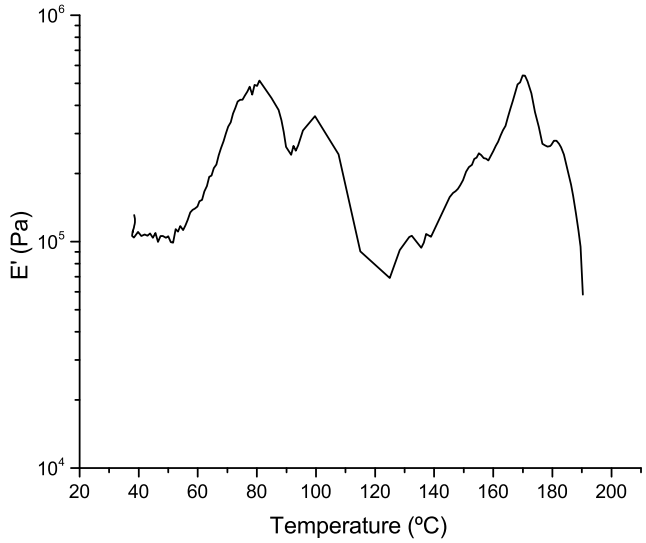


Figure 13: Evaluation of stiffness through a dynamic temperature ramp test (experiment number 4 and frequency of 1 Hz).

5.4 Foaming with the hot-mold equipment

For this experiments it was decided to start with one common polymer concentration and, depending on the results, decide the next one. Therefore, the first trials were carried out with a 10% polymer content. The solutions were heated to 160, 180, 200 and 220 °C during 10 or 15 minutes. The results and future approach could be summarized as follows (figures with all the baked samples can be found in the Appendix, Figures 16 and 17):

- First, it was noted that sodium sulfate negatively affected the foaming result. Thus, it could be observed that for the experiment number one the sample shrank substantially after heating. It was decided that no further baking

experiments should be done using this material since it did not seem suitable for foaming. A similar behavior was detected in other samples with a higher salt content, where the foams obtained exhibited a higher degree of shrinkage.

- It was observed that with lower amounts of sodium hypochlorite denser foams were achieved after baking. On the other hand, with higher amounts of sodium hypochlorite, that is, lower viscosity, the foam was more porous but weak.
- To proceed it was decided to decrease the polymer concentration to 5% for the solutions giving a more compact structure and increase by 5 % for the more porous ones in order to hopefully obtain a stronger foam.

During the second set of bakings, better results were obtained and, apart from the planned experiments, some more were carried out to give a better understanding of some of the results. For the later experiments, the baking time was fixed to 10 minutes and the samples were heated to three different temperatures; 180, 200 and 220 °C. A picture showing all the results can be seen in the Appendix, Figure 17. Hereafter, a summary of the second batch of experiments is given and discussed:

- As expected, the original M10 showed good foaming behavior for a polymer concentration of 5%. Similar foams were obtained for experiments 10 and 12 and the outcome was predictable since low amounts of chemicals were added (20 g of salt and 0.5 %wt of sodium hypochlorite respectively). The foam formed showed good structure but it was still believed that it could be improved by increasing the polymer concentration to 8 %. However, the foaming behavior seems to be extremely sensitive to the concentration since the results were not very good.
- Experiments which produced a good foaming ability were the ones with the lowest viscosity, number 3 and 4, for polymeric concentrations of 5 and 8% for the first one and 20% for the second one. As in the previous experiments, other concentrations were also used but the results were worse than the previous ones. Again, a high sensitivity to polymeric content was observed.
- The results obtained from the other specimens were not as good as the previously discussed. Nevertheless, it did not mean that they were not suitable for foaming but the processing parameters were not optimal.

In these trials, the temperature seemed to be least significant parameter, although more degradation was observed at higher temperatures, it was not drastically influenced the outcome of the results.

5.5 Size-Exclusion Chromatography (SEC)

The results obtained from the SEC was essential in order to verify that the chain-shortening had been successful. Four of the most interesting samples were chosen for analysis. The results are shown in Figure 14.

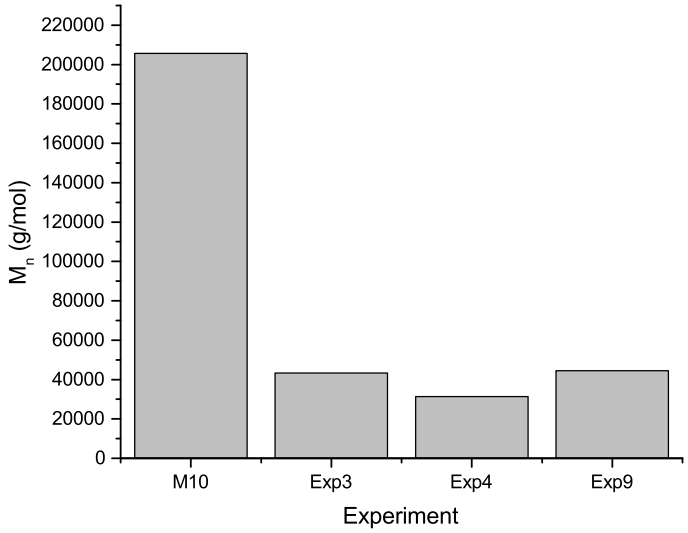


Figure 14: Number average molecular weight (Mn) for some of the samples. No salt was added in the original M10 and Exp 3 and 20 g of this chemical was added to the other two experiments.

Initially, viscosity was used to deduce if the molecular weight of the original M10 was changed due to the hypochlorite treatment. The SEC results confirmed that the more NaClO added, the shorter the chain length became. Additionally, the results shed some more light on the salt effect. As believed, the salt seemed to have a negative effect on the chain shortening process. The chains obtained were even 10% larger with this chemical (difference between Exp9 which has 4% of NaClO and 20g of salt and Exp3, the same but without salt). Also, it was confirmed that between 4 and 8% of NaClO, under the same conditions (Exp4 and Exp9) the difference in molecular weight was not very large. This could point towards a limit where no shorter chains were obtained. It should be mentioned that the values obtained for the polydispersity index were always below 1.8.

5.6 Density

As it is one of the most important parameters in foam characterization, the density was measured for some of the foams obtained and the results are shown and discussed

below. It was measured for five different samples, the ones showing the better foaming ability. The density values are shown in Figure 15. They are arranged in groups which represent the different solutions (number of experiment and polymer concentration) and subgroups indicating if the foams were produced at 180, 200 or 220 °C (1,2 and 3, respectively). The values obtained were between 0.02 and 0.12 g/cm^3. To give a comparison to some commercial foams, these values are slightly higher than EPS (Expanded Polystyrene, 0.012 g/cm^3 [28]), similar to LDPE foams (Low Density Polyethylene, 0.025 to 0.1 g/cm^3 [29]) and lower than PU foams (Polyurethane, 0.14 to 0.71 g/cm^3 [30]).

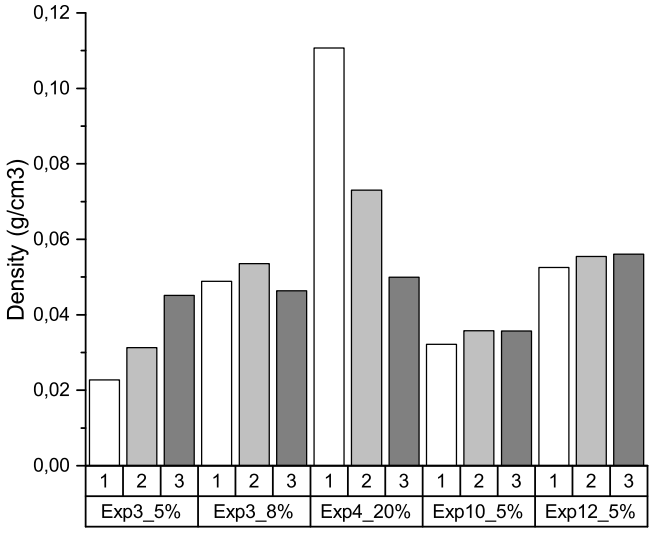


Figure 15: Bar chart with the apparent densities of five different foam structures.

The lowest density was found for Exp3 5 %, the result was not surprising since a good foam but with very low material content resulted from this experiment and polymer content. The foam produced from the solution with highest polymer content, Exp4 20 %, had the highest density, but the density decreased appreciably with increasing temperature.
Even though the temperature seems to have a substantial effect on the final density in case of the specimen from Exp 4, it was still not believed to be one of the critical parameters. Except for this specimen the temperature did not influence the density greatly, figure 15.

6 Conclusions

The project aimed to evaluate the effects of the chain length on the foaming ability of ethyl hydroxyethyl cellulose. The results pointed to a set of clear conclusions.

6.1 Chain shortening of ethyl hydroxyethyl cellulose

Regarding the chain shortening it was concluded that there seems to be a saturation amount of NaClO after which no further reduction in molecular weights was attained. Up to 4 %wt NaClO, the viscosity of the solutions decreased. Additionally, it was observed that salt affects the shortening process in a negative way, giving higher viscosities (directly related with longer chains). Finally, variables such as T_g does not change substantially, hence, it seems not to be directly connected to the molecular weight (in this molecular weight region).

6.2 Foaming ability

EHEC with a reduced molecular weight can produce foams using water as a plasticizer and blowing agent. Due to the shortening of the chain length, higher amounts (up to 20 and 25 %) of polymer are possible in the aqueous solutions. This result could be promising for future applications such as extrusion foaming where higher polymer contents would be beneficial. It can also be concluded that a high sensitivity of polymer content is expected for the foaming and a need to find the processing parameters still exists, but is out of the scope of this study. Finally, salt seems to have a negative effect on the foaming process since higher contents induced a shrinking of the foamed product.

6.3 Size-Exclusion Chromatography

In the last part of the study and with the help of the SEC results, the previous hypotheses could be verified. First, the effect of the chain shortening agent could be supported, that is, the more NaClO that was added, the lower molecular weight. Secondly, it was corroborated the negative effect of salt, obtaining even a 10 % longer chains when this chemical was added. Finally, it was noticed that, after a certain amount of sodium hypochlorite was added, no further chain lowering molecular weight was achieved.

7 Future work

As the different tests were carried out and the properties were evaluated, new questions emerged. However, more time would be needed to look into all of them. Some of all the interesting questions that were not answered are given below and can serve as a possible guide for further studies.

- During the viscosity measurements it was mentioned that the values obtained for experiment 10 (M10 plus 20 g of salt) were surprising. In order to find an explanation to this observation, the experiment should be repeated again. Doing so, it could be verified if the experiment was not done correctly or if there were other factors contributing to the result.

- The baking simulations indicated that the polymer content strongly affects the result. Therefore, trying to find the optimal processing conditions for the different experiments could be interesting and valuable.

- A comparison with HPMC should have been carried out. Unfortunately, it was not possible to do that, thus, it could be a part of a future study. Since the foaming ability of HPMC has been shown to be good in previous studies, it would have been interesting to analyze how a reduction in molecular weight would affect the foaming ability of this derivative and if the previous results obtained could be further improved.

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Appendix

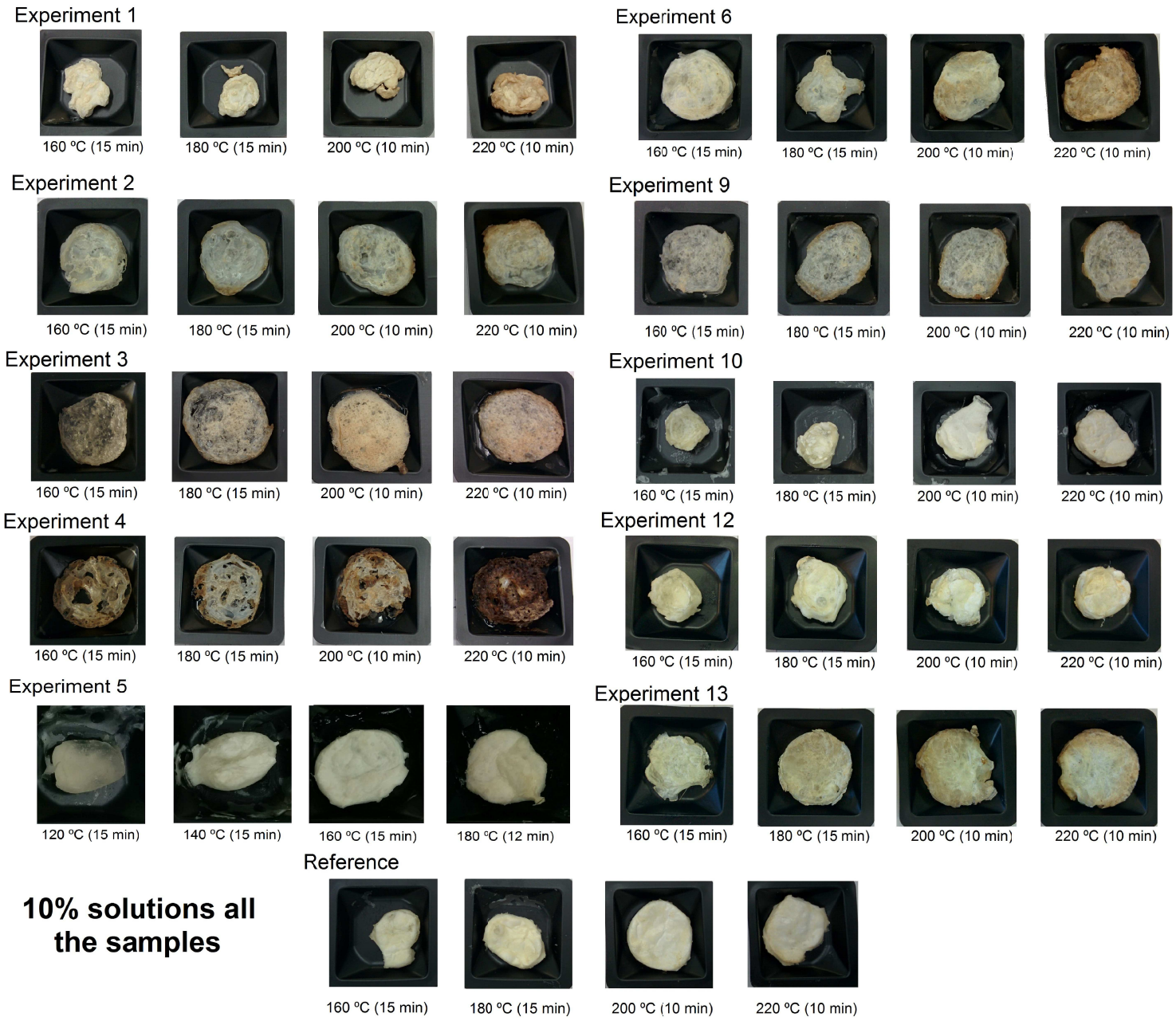


Figure 16: All the baked samples during the first trial.

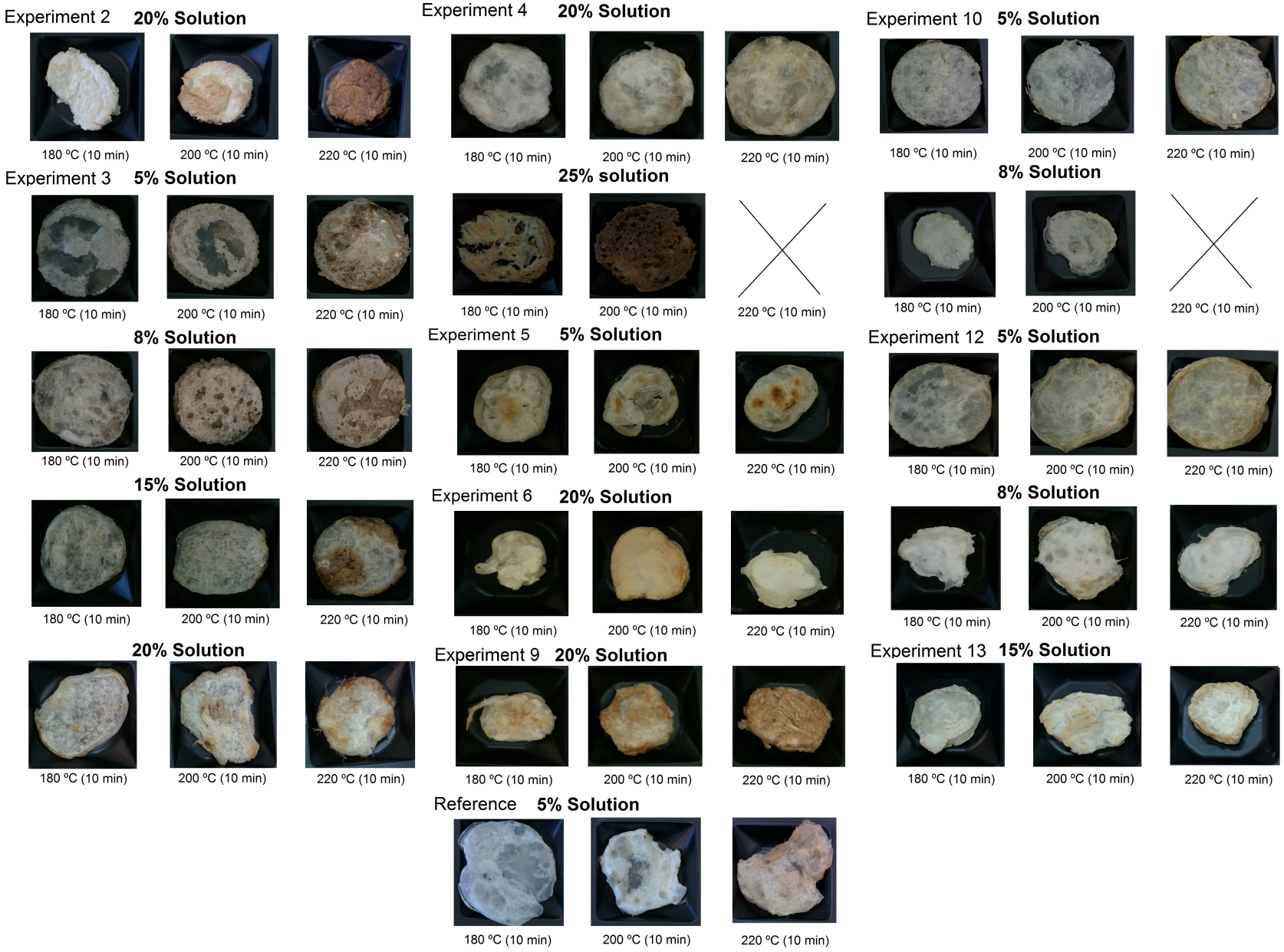


Figure 17: All the baked samples during the second trial.