Modeling of water up-take in superabsorbent systems

Pedro Nuno Lemos Brandão

A Thesis submitted for the degree of
Master of Science in Mechanical Engineering
to the Faculty of Engineering, University of Porto

Supervisor FEUP: Alexandre Miguel Prior Afonso
Supervisor BASF: Andreas Daiss

February de 2017
I would like to express my gratitude to Dr. Alexandre M. P. Afonso for all the help and encouragement. Despite having another project, he was always available for answering my questions, without his support this dissertation would not have been possible.

To Dr. Andreas Daiss from BASF, firstly for the opportunity, also for the physical and chemical knowledge and for giving me the tools needed to complete the purpose of this work.

I must acknowledge the Faculty of Engineering, University of Porto (FEUP), for introducing me to this great opportunity to do my master thesis in BASF.

A special thanks to all my friends from Porto, who kept supporting me all the way and always motivating me to continue.

To my family, for believing in my education, for all the motivation given but also for the all the critics. Without criticism, there is no improvement, and making them proud is the best feeling. I would also like to give a special acknowledgement to my family in Germany. Despite the almost nonexistent previous contact, they received me as a new son, always making me feel at home. There is no such thing as good or bad family, because we cannot choose it, it is only family. But there are good friends, and they will always have a great friend that will always be grateful for all the support, thank you.

Finally, I acknowledge with thanks BASF for funding my work.
Abstract

Superabsorbent polymers are substances that have the ability of absorb high quantities of fluid (up to 300g of water per gram of dry polymer). In fact, there are many types of chemical compositions, different properties and usage conditions, which may improve or not the desirable behavior of each type of polymer.

The implementation on disposable diapers was the main factor for development and production, which made superabsorbent polymers economically viable for the consumer.

Despite being an old technology, from the early 70’s, nowadays are created more types of superabsorbent polymers with improved swelling capacity and velocity, and trying to test all of them in many different conditions in a lab is very expensive and time consuming. So, it is a tremendous advantage to have a numerical model which can predict the performance not only of all the superabsorbents but also a combination of some.

Researchers from BASF developed an OpenFOAM® solver, called diaperFoam, which was able to predict the physical outcome of a superabsorbent system. However, this solver was in its basic form, still not yet validated, and did not had all the features needed for a usable model. Introducing new quantities to improve the model’s predictability was the proposed work for this master thesis.

First of all, understanding all the phenomenon involved in the absorption of liquid was essential to identify what was missing in the old solver version. Also, recognizing the quantities present in the code, which is in a C++ language, was one of the first steps for developing this work.
Adding new parameters and features, and analyze their effect on notice the final results was other step of this thesis.

Several numerical simulations were made to check if the results correspond to the expected outcome. Despite having many quantities and parameters, which can lead to an infinity of simulation cases, some relevant data is presented in this report to better understand the behavior of this material under certain conditions.
Resumo

Polímeros super-absorventes são substâncias que conseguem absorver grandes quantidades de fluido (até 300g de água por grama de polímero). De facto, existem muitos tipos de composições químicas, diferentes propriedades e condições de uso, que podem melhorar, ou não, o comportamento requerido para cada tipo de polímero.

A sua implementação em fraldas descartáveis foi o principal factor de desenvolvimento e produção, o que fez com os polímeros superabsorventes fossem viáveis economicamente para o consumidor.

Apesar de ser uma tecnologia antiga, início dos anos 70, hoje em dia são criados novos tipos de polímeros superabsorventes com uma melhor velocidade e capacidade de absorção, e tentar testas todos estes produtos em diferentes condições num laboratório é muito dispendioso e demorado. Por estas razões, é uma vantagem enorme ter acesso a um modelo numérico que consegue prever a performance não apenas para todos os polímeros, mas também uma combinação de alguns.

Investigadores da BASF desenvolveram um modelo em OpenFOAM®, chamado diaperFoam, que consegue prever uma solução física de um sistema super-absorvente. No entanto, este modelo encontrava-se na sua forma básica, ainda não validado e sem soluções para um modelo passível de ser usado. Introduzir novos parâmetros para melhorar as previsões do modelo for o trabalho proposto para esta tese de mestrado.

Primeiro, compreender todos os fenómenos envolvidos na absorção de líquido foi essencial para identificar o que faltava na versão anterior do modelo. Reconhecer todas as variáveis presents no código, em linguagem C++, foi também um dos primeiros passos deste trabalho.
Adicionar novos parâmetros e analisar o seu efeito foi outro aspecto desta tese.

Foram feitas inúmeras simulações numéricas para verificar se os resultados do modelo correspondem ao resultado final esperado. Apesar de englobar muitas variáveis e parâmetros, que podem levar para um infinito número de casos de simulação, a informação relevante é apresentada neste relatório para uma melhor compreensão do comportamento deste material em certas condições.
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List of Symbols and Acronyms

1D  One-dimensional
2D  Two-dimensional
3D  Three-dimensional
SAP Super Absorbent Polymer
$q_m$ Swelling ratio
$\chi$ Polymer-solvent interaction parameter
$V_1$ Molar volume of solvent
$\rho_0$ Density of the fluid
$M_c$ Length of polymeric chain between crosslinks
$M_n$ Kinetic chain length of the polymerization
$v_{20}$ Concentration of monomer during crosslinking
$c$ Mass fraction of polymer in the gel (gram polymer per gram gel)
$G_0$ Reference elasticity modulus
$G_e$ Strain that is recovered when the stress is removed
$P$ External pressure load applied in the system
$A$ Cross-sectional area
$L$ Length
$\mu; \quad$ Viscosity
$\kappa_D$ Specific permeability
$\Delta P$ Pressure difference
$d_{vl}$ Equivalent volume diameter
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_i$</td>
<td>Sphericity</td>
</tr>
<tr>
<td>$\sigma_g$</td>
<td>Geometric deviation</td>
</tr>
<tr>
<td>$\mu_g$</td>
<td>Weighted geometric mean</td>
</tr>
<tr>
<td>$\Delta V^*$</td>
<td>Specific volume variation</td>
</tr>
<tr>
<td>$\dot{V}$</td>
<td>Volumetric flow</td>
</tr>
<tr>
<td>$K$</td>
<td>Permeability</td>
</tr>
<tr>
<td>$K_h$</td>
<td>Hydraulic conductivity</td>
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<tr>
<td>$\phi$</td>
<td>Porosity</td>
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<tr>
<td>$\phi_0$</td>
<td>Initial Porosity</td>
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<tr>
<td>$\psi_{CK}$</td>
<td>Carman-Kozeny factor</td>
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<tr>
<td>$d$</td>
<td>Sphere diameter</td>
</tr>
<tr>
<td>$L_c$</td>
<td>Length of the streamlines</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Fitting parameter</td>
</tr>
<tr>
<td>$Co$</td>
<td>Courant Number</td>
</tr>
<tr>
<td>$U$</td>
<td>Magnitude of the velocity</td>
</tr>
<tr>
<td>$\delta x$</td>
<td>Cell size</td>
</tr>
<tr>
<td>$\delta t$</td>
<td>Time step</td>
</tr>
<tr>
<td>$p_c$</td>
<td>Convergence order</td>
</tr>
<tr>
<td>$V_{Bl}$</td>
<td>Absolute Volume of Bound Liquid</td>
</tr>
<tr>
<td>$\gamma_{Bl}$</td>
<td>Bound Liquid’s Volume fraction</td>
</tr>
<tr>
<td>$V_{total}$</td>
<td>System’s total Volume</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Thesis Context

Superabsorbent polymers are crosslinked networks of flexible polymer chains. The material is considered an elastomer, capable of large and reversible deformation [1].

They can appear under different names, such as hydrogel, waterswellable polymer, water-absorbent polymer, superabsorbent material and superabsorbent polymer (SAP) [2].

Super absorbent polymer was first produced in 1970s in Japan [3]. These polymers are commonly made by polymerization of acrylic acid blended with sodium hydroxide to produce a poly acrylic acid sodium salt referred to as sodium polyacrylate. This is the most common type of SAP used today [2].

The last years have experienced the appearance of new SAP producers, increasing the market competition in this kind of material. So, it is important to have a good quality product with good properties and have also an attractive price to the customers.

The researching of new superabsorbent polymers is a long process. Not only different chemical compositions can be tested and experimented, but also new processes can be created. All of this needs a huge amount of laboratory work, in order to test the products under specific conditions.
For this reasons, having a reliable model which can predict new solutions, with reasonable accuracy, is a huge market advantage. Instead of testing all the new ideas in the laboratory, the researchers, simulating those new concepts in a numerical tool, could save time and money and even get the information of what chemical composition as more benefits in specific conditions.

A detailed overview on superabsorbents can be found in [3,4].

1.2 Objectives

The objective of this thesis is the development of a numerical tool regarding the water absorption in super absorbent polymers. This tool has the main purpose of helping researchers to understand how the change of some quantities affects the behavior of the polymer, and giving them some more data for new polymer development.

A pre-existing solver, developed by BASF, in an Open Source Field Operation and Manipulation software (OpenFoam®), called diaperFoam served as base to all the new features introduced in this model. The main advantage of using this software is the fact it is free, making it more financially accessible.

1.3 Thesis Outline

This dissertation is divided into seven chapters and one appendix.

In Chapter 2, a literature review on the fundamental definitions and processes is given.

In Chapter 3, the equations and the theoretical background used in the solver is described.

In Chapter 4, a brief description of the features and tools that the OpenFOAM® software provides is presented.

In Chapter 5, is made a sensitivity analysis, in order to guarantee the error inherent to the mesh resolution is minimal.
In Chapter 6, some simulations are described and discussed, and are presented comments about results of the relevant quantities. Also, another feature of the solver, which is the ability of combining different polymers and simulate their behavior as a system, is presented.

In Chapter 7, the main conclusions and the future work it can be done to improve the solver are presented.

In Appendix A, it is presented some figures describing visually the relevant parameters in Chapter 6.
Chapter 2

Literature Review

2.1 Concepts and Definitions

In this subchapter, will be presented some initial concepts and definitions based on the works of Frank M. [2] and Tobita H. [5].

2.1.1 Superabsorbent Polymer - Definition

The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups [3].

The introduction of branches and/or crosslinks endows polymers with further versatility, creating a gel molecule. It is considered to be a crosslinked polymer with very high molecular mass, and as consequence, a gel molecule is insoluble in any solvent under conditions where polymer degradation does not occur [5]. A schematic drawing of a crosslinked polymer network is shown in Figure 1.

The liquid up-take in superabsorbents function by means of a diffusive mechanism. Water moves into a particle of polymer due to the activity of water is initially lower in the interior of the particle. As water diffuses to its interior, the particle volume increases and the polymer chains that form the superabsorbent polymer network must also move, generally in the opposite direction, in order to accommodate the volume of the additional molecules of water [3].
However, this stretching of the polymer chains, as a result of the solvent up-take, has a limited maximum value. Eventually, the force resulting from the elongation balances the force that results from the difference of liquid concentration between the inside and the outside of the particle, and it stops flowing into the particle [3]. The equilibrium depends on the interconnected structure of the polymer in the particle and on the nature of the liquid that diffuses into the particle.

The majority of superabsorbents produced today are partially neutralized polyacrylates. Numerous other polymers have been crosslinked to form water-swellable gels, but no other polymer can provide the high charge-to-mass ratio as economically as poly(acrylic acid) and its salts [3].
2.1.2 Monomers

As mentioned before, good polymer properties can be achieved with high-purity acrylic acid. Besides acrylic acid, in principal all hydrophilic polymerizable substances come into consideration as monomers for superabsorbents. In addition, hydrophobic polymerizable substances can also be used as co-monomers. Important for the superabsorbent effect is the generation of charges along the polymer chains when the superabsorbent comes into contact with aqueous liquids [2].

2.1.3 Cross-Linkers

All compounds with at least two polymerizable double bonds, compounds with a polymerizable double bond and a functional group which is reactive towards the monomers, and compounds with at least two functional groups that can react with the monomers are generally suitable as cross-linkers for superabsorbents [2].

2.1.4 Crosslinked Polymers

An important characteristic of the introduction of crosslinks to linear polymer systems is the formation of a gel molecule. A gel molecule is considered to be a crosslinked polymer with infinite molecular mass, and as a consequence, a gel molecule is insoluble in any solvent under conditions where polymer degradation does not occur [5].

Gel is a molecule that spans the whole reaction system, and therefore, if one chooses one monomeric unit in polymer randomly, as was shown in Figure 2, the probability of choosing a gel molecule must be larger than zero. On the other hand, because the number of polymer molecules in the system could be infinite, the probability of selecting a gel molecule on a number basis could be zero. Therefore, the onset of gelation can be recognized as a point when the mass-average degree of polymerization (chain length) goes to infinity as observed in Figure 2 [5].
2.2 State of the art

2.2.1 Applications

More than 95% of the superabsorbents are used in products related with personal hygiene: infant diapers, adult care articles, and feminine sanitary napkins [2].

Before SAP’s were used, the absorbent cores of diapers consisted of only cellulose fluff or layers of absorbent papers. Besides the swelling capacity, the main difference between these materials is the releasing of the fluid under mechanical pressure. In modern superabsorbents the absorbed liquid can hardly be released mechanically [2].

For this reason, the report will consider the most common aspects concerning the conditions of usage in a standard diaper. However, there are other situations where a superabsorbent polymer can be used such as absorbent pads, artificial snow, sand bags for flood control, medical waste solidification and many more.
2.2.1.1 Diapers

A typical modern diaper consists of a permeable cover layer (coverstock), a distribution system (distribution layer), an absorption layer (absorbent core) and an impermeable outer layer (impermeable back sheet) [2]. The first two are responsible to distribute the liquids over a wide area of the absorbent core, which stores them without any release to the surface of the diaper. Finally, the outer layer is a water-impermeable foil. Improved foils are air-permeable.

The use of SAP in this product is located in the absorption core, which consists in a mixture of cellulose fluff and superabsorbent granules [2]. The cellulose fibers provide good distribution of the liquid in the entire layer but cannot effectively store it themselves.

![Figure 3 - Schematic representation of diapers. Reproduced from Buchholz F. L. [3].](image)
Over the years, diapers became more thin, increasing the density of the core. A reduction in the percentage of fibers was the solution. However, due to the absorption capacity being the main emphasis, superabsorbents were soft and easily deformed. They tended to block the liquid at the point of entry, so an improvement in SAP’s properties was required. Polymers with special properties, such as the ability to swell under an applied load, low or high absorption rates, or unusual particle sizes, led to improved diaper designs [2].

In Figure 3 is represented a diagram with (a) absorbent core of superabsorbent polymer and cellulose fluff sandwiched between the impermeable back sheet and the porous top sheet and (b) layered structure with higher density circular layer of superabsorbent polymer and fluff nearer the back sheet [3].

2.2.1.2 Feminine Hygiene Products

Feminine sanitary napkins are very similar to diaper’s constitution, being the main difference the size of the absorbent core. It has to be much more thin, so the superabsorbent particles used are normally smaller than in diapers. [2]

Superabsorbent fibers are applied as well, due to the fact that menstrual liquids are more difficult to absorb than urine. Protein and blood cells are too large, so they are only adsorbed on the surface, where they impede the absorption of water and dissolved salts.

2.2.1.3 Packaging Food

Ice is used many times to cool and preserve food and other biomaterials. Superabsorbents are also applied in those situations, where is necessary to retain the melted water in order to keep the products relatively dry and, at the same time, preserve some of the cold fluid for food preservation. Usually the SAP is incorporated into a hydrophilic fabric [2].

Due to the fact that these polymers are used in products for human consumption, they have to be approved and they have to follow certain specifications, resulting in some limitations on their chemical composition [6].
Superabsorbent polymers are also used, in smaller quantities, as refrigerants. The swollen gel is frozen and packed in plastic bags to keep perishable foods cold. They can also be used to absorb condensation water in packaging or thicken contaminated liquids in transport containers in hospitals [2].

### 2.2.1.4 Agriculture

In agriculture, the superabsorbents are applied in seed and plant furrows to increase the water-use efficiency. Due to their ability to store water and nutrients for uptake by plants they are used as soil conditioners in sandy soils in arid areas, where the best results are achieved [2].

For this type of application, SAP’s require some special properties. They must swell and shrink under the soil conditions and remain stable for several years and be able to absorb liquid effectively at high salt concentrations [2].

Some compounds can also be introduced in the polymers, such as insecticides or insect growth regulators. In contact with water they are released relatively slow, making it active for long periods of time [3].

### 2.2.1.5 Construction Materials

Superabsorbent can also be used in Civil Engineering. Adding them to concrete or cement, it is possible to achieve improved characteristics, such as lower water stress or increased porosity, to form a composite soil stabilizer for wet soils [3].

In another approach, SAP can also be used as an outside layer on concrete surfaces to prevent the water evaporation, helping the cure process [3].
2.2.1.6 **Electronics and Cabling**

![Diagram of a cable with a water-blocking tape.](image)

*Figure 4 - Wire protected with a water-blocking tape containing superabsorbent polymer. Reproduced from Buchholz F. L. [3].*

Leaking water degrades the performance of fiberoptic communication cables and power transmission cables. Using water-blocking tapes made with superabsorbent material prevents liquids from entering deeper in the cable when the outer plastic cover is damaged. One example of a cable structure with a SAP tape is shown in Figure 4.

2.2.1.7 **Recreational Activities**

There has been some interest in artificial snow for indoor skiing arenas. Mixing SAP with water while freezing it, creates this fake snow that can be used with air temperature at least $10^\circ C$ higher than with snow made only from water [3].

For this application, the polymer has to contain some more chemical compounds to make it viable for usage like silicon oils or fluorocarbon to reduce the coefficient of friction [3].
2.2.2 Market Insights

Since the majority of products that use this polymer have a huge market, it is important to understand the economical dimensions of SAPs. The global super absorbent polymer market was valued at US$ 7.1 Billion in 2014, and is estimated to be slightly over US$ 9 Billion by 2020 [7].

![Global Super Absorbent Polymer Market- By Application, 2014](image)

*Figure 5 - Pie chart of Super Absorbent Polymers by application in 2014. Reproduced from Super Absorbent Polymer (SAP) Market: Global Industry Analysis and Opportunity Assessment 2015 - 2020 [7].*

As showed in Figure 5, the disposable diapers industry accounted for the largest market with more than 74% of the global demand for super absorbent polymer in 2014. It is anticipated to grow with the increasing demand for baby diapers, majorly from the emerging economies.

2.2.3 Manufacturers and Product Names

Table 1 presents some of the main manufactures of this products and their respective names in the market.
Table 1 - Manufactures and trade names of poly(acrylic acids) and polyacrylamides [8]

<table>
<thead>
<tr>
<th>Company</th>
<th>Trade name</th>
<th>Type*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Poly(acrylic acids)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Akzo Nobel</td>
<td>Alcosperse</td>
<td>b</td>
</tr>
<tr>
<td>BASF SE</td>
<td>Dispex</td>
<td>b</td>
</tr>
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<td></td>
<td>Sokalan</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>Hysor</td>
<td>a</td>
</tr>
<tr>
<td>BF Goodrich</td>
<td>Carbopol</td>
<td>d</td>
</tr>
<tr>
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<td>Aqualic</td>
<td>a</td>
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<td>Sanyo Chemical Industries</td>
<td>Sanwet</td>
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<tr>
<td><strong>Polyacrylamides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alco Chemical</td>
<td>Aquatreat</td>
<td>b</td>
</tr>
<tr>
<td>BASF SE</td>
<td>Magnafloc, Zetag</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>Percol</td>
<td>c, d</td>
</tr>
<tr>
<td></td>
<td>Alcoflood</td>
<td>d</td>
</tr>
<tr>
<td>Beijing Hengiu</td>
<td>Hengfloc</td>
<td>e</td>
</tr>
<tr>
<td>Kemira</td>
<td>Superfloc</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>Fennopol</td>
<td>e</td>
</tr>
<tr>
<td>Mitsubishi Rayon Co, Ltd.</td>
<td>Diafloce</td>
<td>c</td>
</tr>
<tr>
<td>Nalco</td>
<td>Ultimer</td>
<td>c, d, e</td>
</tr>
<tr>
<td>SNF Floerger</td>
<td>Aquasorb</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>Flopam</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>Floret</td>
<td>e</td>
</tr>
<tr>
<td>Soleris</td>
<td>Praestol</td>
<td>c, d</td>
</tr>
<tr>
<td></td>
<td>Praestaret</td>
<td>e</td>
</tr>
</tbody>
</table>

* a = superabsorbent; b = dispersant, scale inhibitor; c = flocculant; 
d = thickener; e = retention aid.
Chapter 3

Theoretical Models and Governing Equations

This chapter presents the main theoretical models and governing equations used to describe the behavior of SAP dynamics. This models are theoretical and were used to improve the solver arranging and combining some of their equations. Since all these quantities depend on each other, when considering a combined system of particles, it will be divided in three main sub-chapters in order to introduce firstly the concept of single particle and then the overall system composed by a plurality of them.

3.1 Single Particle Analysis

SAP are in the majority core-shell particles. In order to maintain their shape during the absorption of liquid, the shell has a higher crosslink density than the core. This means that the particle retains most of its liquid in the interior.

3.1.1 Swelling of Superabsorbent Particles

Liquid is absorbed until the difference in chemical potential inside and outside is balanced. This mechanism depends highly in the chemical properties of the SAP [3]: 
\( q_m^{5/3} = \frac{(1/2 - \chi)^2 \text{MC}}{V_1\rho_0 \nu_0^{2/3} (1 - 3\text{MC}/\text{MN})} \)  

(1)

where,

\( q_m \) - swelling ratio;
\( \chi \) - polymer-solvent interaction parameter;
\( V_1 \) - molar volume of solvent;
\( \rho_0 \) - density of the fluid;
\( \text{MC} \) - length of polymeric chain between crosslinks;
\( \text{MN} \) - kinetic chain length of the polymerization;
\( \nu_0 \) - concentration of monomer during crosslinking.

As will be mentioned further on this chapter, different chemical properties of the superabsorbent polymers translate in different mechanical behavior of the system. Parameters such elasticity, permeability and swelling capacity are very affected by these chemical properties.

3.1.2 Elasticity

Superabsorbent particles are polyelectrolyte networks and, like other polymer networks, they are elastic materials. When an elastic material is subjected to mechanical stress, it deforms or strains [3].

The elastic modulus \( G \) is a function of polymer concentration during the absorption:

\[ G = G_0 c^{1/3} \]  

(2)

where,

\( c \) - mass fraction of polymer in the gel (gram polymer per gram gel);
\( G_0 \) - reference elasticity modulus.
Expressing the reference modulus, $G_0$, in terms of the fully swollen modulus in the absence of pressure [3]:

$$G_0 = \frac{G_e}{c_e^{1/3}}$$  \hspace{1cm} (3)

It’s possible to quantify the modulus of elasticity $G_e$, which refers to the strain that is recovered when the stress is removed [3].

Letting $m = c/c_e$, where $m$ is a multiplier ($m \geq 1$) of the equilibrium concentration of polymer, and setting the mass fraction $c$ and $c_e$ to the equilibrium value with load and without any load respectively, it is possible to obtain a value for $G_e$ for that specific load $P$ [3]:

$$m^{9/4} - m^{1/3} = P/G_e$$  \hspace{1cm} (4)

In fact, this modulus varies during absorption. An increase in the swollen volume decreases the concentration of elastic chains, decreasing the elasticity and allowing more deformation caused by a specific load in the system. This phenomenon changes the system’s porosity reducing its value.

### 3.2 System Analysis

SAP’s are capable of absorbing large quantities of liquid fluids spontaneously and rapidly, changing into a gel-like substance.

There are two principal mechanisms of absorbency: the physical filling up of the open space of a porous media and the diffusion of the liquid into the absorbent material itself [2].

In the first one, when the open space forms a connected path throughout the material, it becomes possible to transport liquid into and through the material [2]. The principal
factors affecting the flow may be related by means of Darcy’s law. For steady, slow flow in one direction [3]:

\[
\frac{dV}{dt} = -\frac{\kappa_D A \Delta P}{\mu L}
\]

(5)

where,

\( \frac{dV}{dt} \) - volumetric flow rate;

\( A \) - cross-sectional area of the sample;

\( L \) - length of the sample;

\( \mu \) - viscosity of the fluid;

\( \kappa_D \) - specific permeability of the sample;

\( \Delta P \) - pressure difference driving the flow process.

Many different forces may act on the liquid, including gravity, hydrostatic pressure and capillary pressure. The latter is of great importance in absorbent materials because it’s responsible for the wicking action of the absorbent medium that acts to initially transport the liquid into the dry absorbent material [3].

### 3.2.1 Porosity

Of the many variables affecting the packing of particles, the particle size distribution (PSD) has a major significance to predict the porosity of a packed bed of particles.

It is known that the particles involved in engineering practice are usually not spherical, and particle shape has a strong effect on porosity [9]. In fact, having different sizes of particles in the same system creates a dependency for porosity calculation. Depending on the ratio between the size of those particles, a model to predict the volume occupied was created [9].

Since the particles shape is not spherical, it has to be quantified in terms of equivalent packing diameter, which can be determined by measuring and then relating its size-dependent packing property to the diameter of a sphere as a result of the similarity between spherical and nonspherical particle packings.
Component $i$ should therefore have an equivalent packing diameter $d_{pi}$ which is a function of $d_{vi}$ and $\psi_i$:

$$\frac{d_{vi}}{d_{pi}} = \psi_i^{2.785} e^{2.946(1-\psi_i)}$$  \hspace{1cm} (6)

where,

- $d_{vi}$ - equivalent volume diameter;
- $\psi_i$ - sphericity.

![Diagram](image)

**Figure 6 - Two-dimensional diagram illustrating the random packing structure of nonspherical particles with their size represented by equivalent packing diameters, from Yu and Zou [9].**

If the sizes of all the components in a considered system are represented by their corresponding equivalent packing diameters, then the equivalent packing system will be composed by spherical particles only. As shown in Figure 6, it is considered that the specific volume variation increases mainly due to the joint effect of medium particles.
Assuming a spherical monosized particle packed bed, initial porosity should be constant, generally taking the value of 0.4 for the loose random packing or 0.36 for the dense random packing [9].

Then, using a PSD is possible to get the value of the porosity for non-uniformed sized particles by a prediction in terms of specific volume variation, as shown in Figure 7. As it can be seen, the variation depends on the geometric standard deviation $\sigma_g$, equation (9).

If the geometric mean of a set of numbers $\{A_1 A_2 \ldots A_n\}$ is $\mu_g$, then the geometric deviation is:

$$\sigma_g = \exp \left( \frac{\sum_{i=1}^{n} (\ln \frac{A_i}{\mu_g})^2}{n} \right)$$

(7)

Considering that we are using the weighted geometric mean:

$$\mu_g = \exp \left( \frac{\sum_{i=1}^{n} w_i \ln (A_i)}{\sum_{i=1}^{n} w_i} \right)$$

(8)

With this, $\sigma_g$ is calculated by:

$$\sigma_g = \exp \left( \frac{\sum_{i=1}^{n} w_i \left( \ln \frac{A_i}{\mu_g} \right)^2}{\sum_{i=1}^{n} w_i} \right)$$

(9)

Considering a loose random packing, it is possible to obtain a prediction for the porosity, using the specific volume variation $\Delta V^*$ (Figure 7):

$$Porosity = 1 - (0.6 + (0.6 \times \Delta V^*))$$

(10)
Figure 7 – Specific volume variation vs $\sigma_g$ for particles with the size distribution for a loose random packing. Reproduced from Yu and Zou [9].

However, during the absorption of fluid, the particles can be deformed, when considering an external load on the system. The evolution of the porosity depends on the state of absorption, in the external load applied in the top of the system and in the elasticity modulus, described on equation 11.

$$\phi = \frac{\phi_0}{(1 + P/G)}$$
3.2.2 Permeability

The permeability is a measure of how rapidly liquid flows through the mass of swollen particles [4].

Low permeability means blockage of the gel for further liquid and decreases the system’s swelling ability. Using a diaper as an example, if the passage of fluid is blocked, the diaper can’t fully use its absorption capacity and it may leak [2].

Permeability depends on the particle-size distribution, the free volume of the pores and the connection between them, and the ability of the individual gel particles to maintain their shape in the swelled state under pressure. In other words, it is a function of the porosity, geometry, packing and elasticity modulus of the gel particles [2].

In an experiment initiated by Darcy (1857) concerning water flow through sand, it was established an equation [10]:

$$\dot{V} = -K_h A \left( \frac{dP}{dx} \right)$$  \hspace{1cm} (12)

where,

$A$ - cross section area;

$\frac{dP}{dx}$ - pressure drop.

The constant $K_h$ describes the hydraulic conductivity, which depends on the geometry and fluid properties [10]. In order to turn this parameter independent from the fluid properties:

$$K = K_h \cdot \mu$$  \hspace{1cm} (13)
where,

\( K_h \) - hydraulic conductivity;
\( \mu \) - fluid viscosity.

Making this substitution results in equation (13):

\[
\dot{V} = -\frac{K_h A}{\mu} \left( \frac{dP}{dx} \right)
\]  \hspace{1cm} (14)

Based on capillary flow through beds of spherical particles, the Carman-Kozeny equation predicts permeability values for a wide range of porosity levels with acceptable accuracy:

\[
K = \frac{d^2}{\Phi \psi_{CK}} \frac{\phi^3}{(1 - \phi)^2}
\]  \hspace{1cm} (15)

where,

\( \phi \) - porosity;
\( \psi_{CK} \) - Carman-Kozeny factor;
\( d \) - sphere diameter.

The \( \psi_{CK} \) is a non-dimensional value determined experimentally. Carmen (1937) proposed one of the most widely accepted methods to determine this factor, which implements the concept of tortuosity - ratio between the length of the streamlines, \( L_c \), and the length of the sample, \( L \).

\[
\psi_{CK} = \Phi \left( \frac{L_c}{L} \right)^2
\]  \hspace{1cm} (16)

Where \( \Phi \) is a fitting parameter introducing the effect of the particle’s shape. It assumes the value of 60 or 90 for slab flow or pipe flow respectively. The value of the tortuosity is assumed to be constant, for spherical particles, and is equal to \( \sqrt{2} \).
However, this equation is valid for isotropic porous media only, which means that the system is considered uniform in all directions [10].

3.3 System’s Behavior

The previous parameters influence the swelling capacity of a superabsorbent system. They all depend on each other, starting on the polymer production and ending in the total absorption of a specific system.

Swelling capacity is probably the most important feature for the qualification of a superabsorbent’s performance. In fact, their use in disposable diapers is the main application of SAP, so it is important to relate superabsorbent’s behavior under certain conditions, such as external load and salinity in the absorbed liquid.

3.3.1 Swelling Under Load

The swelling under pressure is a factor to consider for diapers usage. It is expected improved results for superabsorbents which are less easily deformed and deswelled by the load (ex. weight of a baby).

As mentioned before, the elasticity of a SAP particle is decreased during the process of swelling and having an external pressure results in more deformation. This reduces porosity, due to the rearrangement of the deformed particles in the system. As a result, permeability decreases, blocking the fluid penetration in all the system. In other words, the liquid is transported through the system by capillary forces as long as the porosity is high enough and the pores between the particles are connected [4].

The normalized swelling capacity of superabsorbent polymer as a function of the elastic modulus of the gel applied pressure is represented in Figure 8.

In general, the absorbency under load decreases as the modulus of the swollen gel decreases.
However, not only the mechanical features affect the desired behavior of a superabsorbent polymer. The fluid properties also have an important role in the system performance.

Figure 8 - Normalized swelling capacity of superabsorbent polymer as a function of the elastic modulus of the gel applied pressure. Reproduced from Buchholz F. L. [3].
3.3.2 Salinity

The existence of some salts has to be considered also in diapers. To mimic the composition of urine, it is often used a solution of water with 0.9% NaCl in the experimental samples. In Figure 9 is described one example how salt concentration of the absorbed fluid affects the equilibrium swelling without any load applied to the system.

However, the effect of salinity decreases with the increasing of the pressure. Figure 10 shows that the swelling capacity increases with the decreasing salt concentration in the liquid, at small loads. This phenomenon results from the larger osmotic pressure of the salt solution. For higher loads, that difference is less significant.

At higher salt concentration, the concentration of polymer in the gel phase results in larger modulus, and then more difficult to compress, explaining the small difference of absorbency with different loads in sample (d).
Figure 10 - Gel swelling versus applied load for the highest crosslink density sample in various concentrations of NaCl solution: (a) 0.225%, (b) 0.45%, (c) 0.9%, (d) 1.8%. The sample is 33 mol% neutralized. Reproduced from Buchholz F. L. [3].
Chapter 4

Numerical Methods and Software Description

In this chapter it will be provided a brief sum of the software’s properties and features used for this thesis: OpenFOAM® - Open Source Field Operation and Manipulation.

4.1 Introduction

First of all, this software is the most used open-source tool for Computational Fluid Dynamics worldwide. It is first and foremost a C++ library, used primarily to create executables, known as applications. Also, it has a tremendous advantage in the constant improvements and new features introduced by talented people around the world. For this reason, the software develops faster than the others which makes it extremely useful. To easily understand how this works, a simulation task can be divided in three different steps, as showed in Figure 11.

![Figure 11 - Overview of OpenFOAM® structure from OpenFOAM Tutorial Guide [13].](image-url)
In the following subchapters it will be explained some of the most common main features used to run simulations, based on the OpenFOAM® User Guide [12] and OpenFOAM® Tutorial Guide [13].

4.2 File Structure

The basic directory structure for a OpenFOAM® case, that contains the minimum set of files required to run an application, is shown in Figure 12.

![Figure 12 - Case directory structure, from OpenFOAM User Guide [12].](image)

4.2.1 Constant Directory

This directory contains the description of the case mesh (e.g. geometry, number of cells and boundary conditions) and files specifying physical properties for the concerned case (e.g. transportProperties) [12].
4.2.2  System Directory

The parameters related to the solution procedure itself are located in this directory. It contains at least 3 files: `controlDict` - control parameters such as start/end time, time step, write interval and others; `fvSchemes` - selects the discretization schemes used in the solution; and `fvSolution` - sets up the equation solvers, tolerances and other algorithm controls.

4.2.3  Time Directories

This refers to directories, usually named after the simulation time they were written, that contain all the desired information for each write interval specified in the `controlDict` file previously mentioned. Note that OpenFOAM® fields must always be initialized, even when the solution does not strictly require it. Usually simulations start at time $t = 0$, so the initial conditions have to be stored in a directory named 0.

After simulation, the time directories will be used by post-processing software to join all the information written in output variable files.

4.3  Pre-processing

Cases are setup in OpenFOAM® by editing case files. A case being simulated involves data for mesh, fields, properties and control parameters [13].

4.3.1  Mesh generation

This software always operates in a 3 dimensional Cartesian coordinate system and all geometries are generated in 3 dimensions, even for 1D and 2D cases [13].

The mesh generator supplied with OpenFOAM®, `blockMesh`, generates meshes from a description specified in an input dictionary, `blockMeshDict` located in the `constant/polyMesh` directory for a given case [13].
Each block of the geometry is constituted by a number of cells in each direction. The mesh generation also can be used to define the type of dimension solution it will be used (3D, 2D or 1D). Increasing the number of cells increases also the mesh refinement and the time spent for the simulation.

After the blocks are properly defined it is necessary to set up the boundaries, which are represented by the faces of the geometry.

An example of a block structure of the mesh is represented in Figure 13.

### 4.3.2 Boundary Conditions

A boundary is generally divided into a set of patches (regions), which may include one or more enclosed areas of the boundary. Each patch has a keyword associated to it, describing the interaction with the virtual exterior of the domain, called boundary types.

*Figure 13 - Example of a block structure of the mesh. [9]*
There are more than 70 types of boundaries, being the most common the basic ones like: *fixedValue*, *fixedGradient* and *zeroGradient*. For the interested reader, consult the user guide [12].

### 4.3.3 Discretization and linear-solver settings

OpenFOAM® is based on the Finite Volume Method. In general, differential equations must be discretized in order to solve them numerically. This results in a set of non-linear algebraic equations. The exact solution of this set of equations is different from the exact solution of the differential equations. The resulting difference depends on the discretization method used and on the resolution of the discretization and is called discretization error. A direct solution of the set of non-linear algebraic equations is impossible in most of the cases. Therefore, iterative methods are used, which rely on the solution of a locally linearized set of equations. The difference between the exact solution of the set of non-linear algebraic equation and the solution computed by the iterative method is called residual error or just residual. Both errors the discretization error and the residual error add up to the overall error of the numerical solution of a set of differential equations. It is important to control the numerical error by an appropriate choice of the discretization method and the resolution of the discretization as well as by checking carefully the residual error. In OpenFOAM®, the user specifies the choice of finite volume discretization schemes in the *fvSchemes* dictionary and the linear equations solvers and tolerances in the *fvSolution* dictionary, both in the *system* directory.

### 4.3.4 Control

As mentioned before, the input data concerning the time control and the reading/writing can be found in the *controlDict* dictionary located in the *system* directory. While setting all the simulation’s time specific values, there is one called *maxCo* (maximum Courant number), which is needed to achieve temporal accuracy and numerical stability when running the solver. The Courant number is defined for one cell as:
\[
Co = \frac{\delta t |U|}{\delta x}
\]  

(17)

where \( \delta t \) is the time step, \(|U|\) is the magnitude of the velocity through that cell and \( \delta x \) is the cell size in the direction of the velocity. A Courant number of less than 1 is required everywhere for a time-accurate solution of a flow problem. Therefore, the time step \( \delta t \) is chosen based on the worst case: the max \( Co \) corresponding to the combined effect of the largest flow velocity and small cell size. It is common to use an adjustable time step feature to save computation, where a new time step is calculated for each time instant, never exceeding the imposed value of \( maxCo \) [12].

### 4.3.5 Running an Application

After setting all the desired pre-processing features, the solver can be executed and do the simulation. In one hand it can be done as a foreground process, where the simulation’s progress can be seen in the terminal window. On the other hand, it can work as a background process, allowing additional commands before it is completed [12].

It is important to say that if any changes are made in the source code of the solver, it is mandatory to re-compile it, otherwise the simulation does not account for the changes made. If all the changes are in the run directory, there is no need to compile again to work properly. This is why, in order to have a user friendly code, it’s important to keep all the input files in the run directory.

### 4.4 Post-Processing

When the simulation ends, the results are written in the time directories. They can be viewed using paraFoam, that uses the open-source software ParaView to compile all the information related to the time directories.
This software allows to see interactively all the simulation results as line, contour plots or videos. It displays the geometry with a grade of colors that correspond to a specific value. An example is showed in Figure 14.

![Colorful grade example](image)

*Figure 14 - Example of the colorful grade presented in ParaView, OpenFOAM User Guide [12]*

The *ParaView* software can also export data files with the fields’ values for each time step and create vector plots for any location of the geometry.
Chapter 5

Sensitivity Analysis and Numerical Error

In the present chapter the influence of the mesh resolution on the numerical error is analyzed in order to specify an adequate mesh resolution for all further calculations.

5.1 Mesh Refinement Study

Using this kind of software to process numerical simulations creates an inherent error associated to the results. So it is important to guarantee that this error is irrelevant compared to the error associated to the model itself.

To evaluate the error of numerical simulation, concerning the mesh resolution, it was used the Richardson extrapolation method. Through extrapolation, this method is able to estimate the discretization error for a specific solution value $\phi$, based on the values of the solution variable obtained for different mesh resolutions.

If a solution variable is calculated with three different resolutions and each resolution is finer by a factor of 2, the convergence order ($p_c$) of the discretization scheme and the extrapolated value of the solution variable for an infinitely fine resolution can be calculated by [14]:

$$
p_c = \frac{\log \left( \frac{\phi_{2n} - \phi_n}{\phi_{4n} - \phi_{2n}} \right)}{\log 2}
$$

(18)
\[ \phi_{\text{extrapolated}} = \phi_{4n} + \frac{\phi_{4n} - \phi_{2n}}{2PC - 1} \]  

(19)

The discretization error can then be calculated by the difference between the extrapolated value and the value obtained for a given resolution. The error is dependent on the solution variable that is considered.

In the present work, the overall volume of water bound to the polymer \( V_{Bl} \) was used to estimate the discretization error, as is shown in Table 2.

<table>
<thead>
<tr>
<th>Mesh</th>
<th>Number of cells</th>
<th>( V_{Bl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>3.3622 * 10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>3.3365 * 10^{-5}</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>3.3279 * 10^{-5}</td>
</tr>
</tbody>
</table>

This value was calculated with the same load applied to the system, the same polymer and the same time of measurement, 689.5 Pa (0.1 psi) - pressure load used in the experimental method, Polymer 1 and 5 min respectively.

It is noticed that the variation of the \( V_{Bl} \), which is the absolute volume of bound liquid (\( V_{total} \times \gamma_{Bl} \)), decreases as the number of cells increases. The relative error for the “Mesh 1” it is calculated in the Table 3.
Table 3 - Obtained error using equations (18) and (19) for Mesh 1

<table>
<thead>
<tr>
<th>$V_{Bl}$ (Mesh 1)</th>
<th>$V_{Bl}$ (extrapolated)</th>
<th>$p_c$</th>
<th>$\varepsilon_r$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.3365 \times 10^{-5}$</td>
<td>$3.3375 \times 10^{-5}$</td>
<td>1.58</td>
<td>1.1614</td>
</tr>
</tbody>
</table>

It can also be seen in Figure 15 that the overall values, obtained when the liquid is fully absorbed by the polymer, somehow are independent of the mesh resolution chosen.

![Graph](image)

*Figure 15 - Different mesh resolution for the Bound Liquid's Volume Fraction.*

After this analysis, the **Mesh 2** was the mesh resolution used for this thesis, so the error caused by the numerical simulation is below 1%.
5.2 Comparison to Experimental Data

There are some experimental data that can be used to compare the results from numerical simulation. However, the experimental data used in this thesis, only concerns about the amount of water in the system after swelling and, since this model as many parameters to take in account, it may not reflect the exact same conditions the experiments were made.

As will be mentioned in the next chapter, the results shown in this report were simulated with a velocity flow imposition boundary condition. However, in the experimental results, it was used a drainage pressure to get the fluid flowing through the system. So, in this comparison, it will be used also a pressure imposed flow for the numerical simulation, in order to compare both numerical and experimental data.

Figure 16 - Comparison between numerical and experimental data.
Figure 16 shows a similar behavior between the two methods. However, there is a difference in the stabilization value, which can be caused by the missing information about the properties of the polymer used in the experiments.
Chapter 6

Results and Discussion

6.1 Introduction

In this chapter, it will be presented some numerical results using diaperFoam solver, with all the updates done during this thesis. It is divided in two sub-chapters, one concerning the most relevant output parameters and the other refers to how the variation in some parameters affects them.

The results were simulated for specific conditions, referred to in the beginning of each sub-chapter, to try to mimic somehow the conditions of usage in a diaper. Since the presently used model is still under development, the results will be analyzed in the light of being realistic or not.

Since the information regarding the entire system is a weighted average of all the small volumes (cells), sometimes it will be presented information about that partial volume, instead of the entire geometry.

Figure 17 - Boundary conditions and reference partial volume used.
Figure 17 presents the boundary conditions that are used in the numerical simulation of the next results and show position of the reference partial volume that is used in the analysis.

### 6.2 Quantities to be analyzed

As mentioned before, there are many relevant variables and parameters necessary in this particular solver. However, since this is a tool for the development new polymers, understanding how physical and chemical properties affect the polymer’s behavior is vital.

#### 6.2.1 Simulation Setup

Table 4 represents the used parameter values that have been used within for the simulations. This values were used to try to mimic somehow real conditions of usage.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value Used</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>0.01</td>
<td>Height of the Geometry [m]</td>
</tr>
<tr>
<td>Press</td>
<td>5000</td>
<td>Pressure [Pa]</td>
</tr>
<tr>
<td>tpp</td>
<td>0.38</td>
<td>Type of packing - medium</td>
</tr>
<tr>
<td>qmaxout/qmaxin</td>
<td>0.0375/0.121</td>
<td>Maximum Swelling Fitting Curve</td>
</tr>
<tr>
<td>r0</td>
<td>280e-6</td>
<td>Initial radius [m]</td>
</tr>
<tr>
<td>endTime</td>
<td>2000</td>
<td>Time of simulation [s]</td>
</tr>
<tr>
<td>boundary</td>
<td>1.66e-8</td>
<td>Velocity Imposed Flow [m/s]</td>
</tr>
</tbody>
</table>
6.2.2 Bound Liquid

The bound liquid refers to the liquid bound to the polymer. It is probably the most common property used to compare different diaper systems.

The results shown in Figure 18 and Figure 19 were taken from a numerical simulation over 2000 seconds. In one hand, the first one concerns the entire system’s volume, and it is seen that as the polymer takes the liquid, the rate of absorption stabilizes when approaching the maximum swelling capacity. In the other hand, the second one analyses only one partial volume, which corresponds to one “cell” located at 90% of the total initial height of the considered geometry (near the top). It behaves similarly to the previous, when liquid reaches this partial volume it has a fast absorption, stabilizing when it approaches the maximum swelling capacity.

![Graph of System's bound liquid volume fraction over time.](image)
**Figure 19** - Partial Volume bound liquid volume fraction over time.

**Figure 20** - Comparison for the liquid volume fraction between different polymers over time.
The Figure 20, represented below, compares two different polymers. **Polymer 1** has a lower maximum swelling capacity than **Polymer 2**.

### 6.2.3 Porosity

As mentioned before, a broader particle size distribution means a smaller porosity of a fixed bed of superabsorbent particles. Besides the particle size distribution, also the shape of the particle has an impact of the porosity of the system. In case of spherical particle, the shape will change under an external mechanical load. The shape change will be affected by the Young’s modulus of the particle. As liquid is absorbed, the Young’s modulus of the polymer decreases.

This means that the porosity of a fixed of superabsorbent particles will change under load with the degree of swelling of the particles. Figure 21 shows the Young’ Modulus decreasing over time and the consequent decreasing of porosity.

*Figure 21 - Porosity and Young’s Modulus comparison over time.*
6.2.4 Deformation

Since the most common use of superabsorbent polymers is their incorporation in diapers, it makes sense to consider an external load compressing the system (e.g. baby’s weight). That causes a deformation and, as consequence, a reduction of the porosity of the fixed bed of particles and a reduction of the maximum swelling capacity of the polymer.

Figure 22 shows the huge dependency of these two quantities, deformation and porosity.

![Figure 22 - Deformation and Porosity over time - Reference Partial Volume Analysis.](image-url)
6.2.5 Degree of Swelling

The degree of swelling is the liquid volume that is absorbed per polymer mass relative to the maximum of liquid volume that can be absorbed per polymer mass. It is an indicator of the polymer's swelling state. Figure 23 presents the degree of swelling over time. Values close to 1 mean that the polymer is almost saturated with liquid.

![Figure 23 - Ration between swelling rate and the maximum swelling over time - Reference Partial Volume Analysis.](image)

6.2.6 Permeability

Permeability is also a relevant quantity to analyze. Higher permeability means the flow of liquid occurs with low levels of resistance, allowing the liquid to penetrate faster in the system. It depends essentially on the porosity and on the radius of the polymers' particles.
Figure 24 refers to the evolution of permeability over time. The permeability starts to increase when the liquid front is reaching the partial volume, at an initial height of 90%. While the swelling reduces the Young’s modulus of the particles, thus increases the deformation of the particles and reduces the porosity of the fixed bed, the swelling of the particles leads also to larger particle diameters.

Overall the effect of the particle diameter increase on the permeability of the fixed bed is overcompensating the effect of the fixed bed porosity decrease. It must be mentioned that other effects like leakages of loosely crosslinked gel out of the superabsorbent particles may lead to a substantial reduction of the fixed bed porosity. Such effects are not considered in the present model.

![Figure 24 - Permeability over time - Reference Partial Volume Analysis.](image-url)
6.3 Affecting Quantities

Another interesting aspect would be to see how changing some physical parameters affects the behavior of the system.

6.3.1 External Load

The swelling under pressure is a factor to consider for diapers usage. The external load applied compresses the system and reduces porosity and permeability, decreasing the velocity of absorption. Figure 25 shows the evolution of the system considered for different pressure loads. It presents the values for the ratio between the volume and the maximum volume the system would have without any load.

*Figure 25 - V/Vmax over time for different pressure loads.*
6.3.2 Radius

The *diaperFoam* solver uses a particle size distribution to calculate the porosity and the average radius, which will be used to calculate the permeability. It can happen that two distinct PSDs have the same value for porosity, but different value for the average radius of the particles.

If it is analyzed, instead of the entire system, a single partial volume, there are some differences, especially in the velocity of absorption, Figure 26.

![Figure 26 - Bound Liquid Volume Fraction for different particle initial radius over time.](image)

For bigger radius, the velocity of liquid absorption increases in the first instants. This can be easily explained by the fact that the initial permeability has a higher value for bigger particles’ radius. Figure 27 presents the initial permeability values for each value of initial radius used in the simulations.
6.3.3 Porosity

As mentioned before, the porosity is calculated based on a PSD. The solver calculates the geometric standard deviation, $\sigma_g$, that will be used to calculate the porosity. If $\sigma_g = 1$, it means that the distribution is composed only by particles of the same diameter. In other words, it is a spherical monosized particle packed bed, which for loose random packing has the maximum value of 0.40 for porosity (40% of the system’s volume is interstitial volume).

For higher values of $\sigma_g$ increases the range of particles in the PSD, decreasing the porosity.
Figure 28 shows the different evolutions of the system within different PSD geometric deviations. For wider distributions ($4 < \sigma_g < 5$), the differences are not so significant, since the porosity is not highly affected for this range of deviation (Figure 7).

### 6.4 Combining Different Polymers

#### 6.4.1 Introduction

This chapter introduces another feature added to the solver, which is the possibility to combine polymers with different properties. It will be analyzed 1 example concerning two different scenarios.
It was seen previously that the initial average radius in a distribution has an effect in the velocity of liquid’s penetration in the system. It will be compared two different cases, Case 1 and Case 2, for systems with different initial average radius, described in the Figures 29 and 30.

The system is divided in half, and each half has different initial average radius, 300\(\mu m\) and 600\(\mu m\). Case 1 and Case 2 differ in the position of the layers, in Case 1 the bigger radius is in the top and in Case 2 is the opposite situation.

The objective is to analyze both scenarios and realize if it brings any advantage for this type of study.

**Figure 29 - Case 1 description.**

**Figure 30 - Case 2 description.**
6.4.2 Simulation Setup

Table 5 represents the used parameter values that have been used within for the simulations.

Table 5 - Values used for this simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value Used</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>0.01</td>
<td>Height of the Geometry [m]</td>
</tr>
<tr>
<td>Press</td>
<td>5000</td>
<td>Pressure [Pa]</td>
</tr>
<tr>
<td>tpp</td>
<td>0.38</td>
<td>Type of packing - medium</td>
</tr>
<tr>
<td>qmaxout/qmaxin</td>
<td>0.0375/0.121</td>
<td>Maximum Swelling Fitting Curve</td>
</tr>
<tr>
<td>r0</td>
<td>280e-6</td>
<td>Initial radius [m]</td>
</tr>
<tr>
<td>endTime</td>
<td>2000</td>
<td>Time of simulation [s]</td>
</tr>
<tr>
<td>boundary</td>
<td>500</td>
<td>Pressure Imposed Flow [Pa]</td>
</tr>
</tbody>
</table>

6.4.3 Results

Analyzing Figure 31, it can be detected a slight difference between both situations. In the two cases, the water absorption converges to the same value, due to the fact that both have the same swelling capacity, the only quantity that changes is the initial average radius. However, it is noticed a faster absorption in Case 1, since the top layer has higher permeability, the liquid flows faster into the system porous media.
Figure 31 - Bound Liquid Volume fraction over time for Case 1 and Case 2.

Figure 32 - Bound liquid volume fraction for the bottom partial volume over time.
To confirm that the liquid has a higher penetration velocity, Figure 32 analyzes the partial volume correspondent to the bottom of the system. In fact, in Case 1, the fluid reaches the bottom much faster than in Case 2.
Chapter 7

Conclusions and Future Work

7.1 Conclusion

The main objective for this thesis was to improve and develop a pre-existing solver, diaperFoam, and analyze the results given by the simulations. It was presented the numerical simulated data for the most relevant quantities and parameters.

The main improvement was the introduction of the porosity based on a particle size distribution. Allied to the addition of the concept that particles decrease their elasticity as they absorb liquid, the solver can now predict the evolution of the porous media during absorption.

Also, the ability of combining polymers is an important improvement for this solver. Different layers with different physical and chemical properties, can now be simulated.

However, during this work, some difficulties relating the permeability were permanent. During the swelling, the polymer particles became more fragile, due to the chains stretching, which can crack the surface and release gel into the porous media. This gel behaves like liquid, but has still swelling capacity. So, in reality, depending on innumerous conditions, some particles crack and the gel mixes itself in the liquid and in gel from different particles, which can be in different stages of swelling. For this reasons it is extremely difficult to create a model to predict the system’s behavior for this conditions.
7.2 Future Work

There is still a lot of work to do before making this solver in a completely reliable tool for industrial use. The model is still not validated and the constant need of experimental data turns the development of this solver extremely time consuming.

The creation of a model which analyzes only the behavior of a single particle was an important first step towards the final goal. However, there is the need, again, of experimental data regarding only single particles to validate the model to all the polymers.

Then, understanding how physical conditions reflect in a single particle’s behavior, the issue in the permeability, described previously, could be corrected. The blocking of liquid, by decreasing drastically the permeability, could be noticed and avoided/accomplished, depending on the desired behavior.

Thirdly, arranging the solver for 3D simulation is also important for design studies. For example, a numerical tool that can predict, also, the distribution of liquid in a diaper for some different geometries.

Finally, once the code is validated and is able to attend all the user’s needs, it could be created an optimizer. With this, not only the behavior of the polymers was predicted, but also the “perfect” polymer or a combination of some could be given for each specific situation.

Overall, it is still needed a lot of improvement for a reliable model and having these amount of quantities and parameters to take in account, makes this model highly dependent on experimental results.
References


[6] Title 21 - Food and Drugs, Chapter I - Food and Drugs Administration, Department of Health and Human Services, Subchapter B - Food for Human Consumption Part 177, Indirect Food Additives: Polymers, 2016


Appendix A

Visual Data - Relevant Quantities
Bound Liquid - 500 s

Figure A 1 - Bound Liquid - t=0.

Figure A 2 - Bound Liquid - t=500s.
Porosity - 500 s

Figure A 3 - Porosity - t=0.

Figure A 4 - Porosity - t=500s.
Permeability - 500 s

Figure A 5 - Permeability - t=0.

Figure A 6 - Permeability - t=500s.
Radius - 500 s

Figure A 7 - Radius - t=0.

Figure A 8 - Radius - t=500s.
Young’s Modulus - 500 s

Figure A 9 - Young’s Modulus - t=0.

Figure A 10 - Young’s Modulus - t=500s.