

Biodegradable composites derived from silica cryogel and cellulose

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1. INTRODUCTION

In the last decade there has been an intensified interest towards environmental friendly materials due to the difficulties managing solid waste disposal and the drastically decreased number of available landfills. Therefore, in recent years the attention is turned to an alternative type of material, which does not require recycling. These materials are the so-called biodegradable materials, which can be decomposed by living organisms. [1] This feature enables them to be used in a wide range of applications without causing environmental affliction. There are several biodegradable polymers, the most important ones are derived from natural sources. These natural sources may be recycling waste based on cellulose or starch. Their properties are not up to par to their conventional polymer counterparts, thus attempts are being made to reinforce these materials. The most obvious solution seems to be the formation of composite systems where the favorable properties of two or more materials are combined. When a composite material is synthesized from biodegradable starting materials the resulting material will also possess these features. The typical reinforcing secondary phases are ceramic powders, which can considerably improve the mechanical and thermal properties of polymer matrix.

In the present thesis I would like to explore the idea of using the composite of a biodegradable, biocompatible cryogels and reusable cellulose fibers. The aim of this research is to prepare a light, insulating thin composite layer. The cellulose fibers provide the matrix of composites and the silica cryogel particles the reinforcing secondary phase. The gels dried under cryogenic conditions are pellets or flakes due to the freeze drying in vacuum. Thus, a continuous phase is required to get a monolith system. The cellulose is a natural biodegradable polymer, moreover the cellulose fibers can be fabricated from wood waste. The cellulose has a very low density and its thermal insulation property is one of the best from the polymers.

The application of the silica cryogels in insulating composites can be confirmed by hierarchical porous structure of the cryogels, their typical porosity is 40-70 %. The cryogels possess generally large specific surface area and very low thermal conductivity. From the inorganic solid particles, the SiO_2 has one of the best thermal insulation ability. [2] The silica aerogel can also be used as a secondary phase in the insulating composite system but its procedure, the supercritical drying is more expensive than freeze drying.

Our syntheses were always conducted in a solution because the application of solution provides a lot of tools and possibilities of tailoring the required systems. The solution techniques have generally based on sol-gel chemistry. In the solution techniques, various additives can be used. The main role of these additives, is to improve the connection between matrix, the cellulose fibers, and the reinforcing phase i.e. the SiO_2 cryogel particles. The most important additives proved to be in our experiments the aqueous solution of NaOH and carbamide, which are applied to treat the fibers and raise their reactivity. The other worth mentioning additive the hydroxyethyl cellulose, that is able to react with OH surface groups of silica cryogel by means of its OH groups.

2. LITERATURE

2.1 Cellulose

In the modern world with an increase in interest of environment friendly materials, cellulose shows a lot of potential as an ingredient in biocompatible and biodegradable materials due to its renewability, low cost, non-toxicity and relatively high thermal and chemical resistance. The cellulose is available in nature at a high volume, since plants produce more than 10 billion tons per year [3]. The main problem with its effective usage comes from the fact that it usually forms a highly crystalline supramolecular structure through hydrogen bonds. The cellulose shows a persistent chain conformation and close packing, with a high amount of inter- and intramolecular hydrogen bonds. This structure results in high resistance against dissolution or smelt, thus limiting its use cases significantly.

Due to its limited solubility in standard solvents, there have been multiple experiments to develop a solvent mixture that can effectively dissolve the cellulose into glucose, sorbitol, ethylene glycol, synthetic gases, aromatic hydrocarbons and furan compounds. Different type of solvent mixtures can dissolve cellulose fibers to various degrees. One such solvent system is alkali/urea mixture studied due to its relatively low cost and environmental friendliness. During the treatment the OH⁻ ions of the NaOH can break the hydrogen bonds inside the cellulose, with the hydration shell of Na⁺ assisting in the process. While urea does not directly interact with the cellulose fibers, it aids the process by forming a hydration coat around the dissolved chains [4]. For these reasons P. Piltonen and his team tried the formation of all-cellulose composite materials (composite, where both the matrix and reinforcement phase are cellulose) by partially dissolving pulp fibers in a NaOH-urea mixture successfully.

These partially dissolved cellulose fibers can be used to form composite materials with other materials like the highly porous solid materials such as cryogels.

2.2 Type of cellulose fibers

Generally, when discussing fibers to be used as reinforcements in composite materials, two main groups of fibers have to be mentioned: natural and synthetic fibers. Traditionally most composite systems used artificial fibers for the reinforcement of materials, such as polymers, carbon or glass. There is a wide range of variety in the polymer fibers, like polyethylene, polyvinyl acetate, aramid, carbon etc. Although the mechanical properties of such fibers are good, due to growing concerns of the environmental impact, multiple researches make a lot of effort to substitute the synthetic fibers by natural fibers, creating bio-composites. Besides bio-

compatibility and biodegradability, the reduction of cost and the abundance of the materials also makes them desirable substitutes for artificial fibers [5].

Natural fibers can be further divided into three subcategories, these are: plant based fibers, animal fibers and mineral fibers. Here I would like to mainly discuss the plant based fibers. The most widely used plant based fiber is cotton, which is grown inside the seed of genus *Gossypium*. Chemically, cotton consists of 82.7 wt% cellulose, 5.7 wt% hemicellulose and 0.6 wt% wax [6], which makes it the purest source of cellulose in nature. Although some sources mention even higher w/w% of cellulose in cotton (around 88 – 97%). Apart from the textile industry, they are also used in some composite materials as reinforcement phase. This use case was investigated by a Russian research group, where through sol-gel process a cotton-TiO₂ composite was synthesized [7].

There is a transition between synthetic and natural fibers called regenerated fibers, where the natural source is chemically treated to form a new material. One of the most important and widely used regenerated fiber is viscose (the viscous liquid used during the procedure is the origin of its name), which is prepared by treating cellulose fibers, usually in the form of biomass, with a solution, consisting of sodium-hydroxide and carbon-disulfide. Viscose shows advantages of both natural and artificial fibers, and is already used for reinforcement of composites, like the conductive polypyrrole-viscose composite synthesized by a Chinese research group [8]. During the procedure most of the hemicellulose is removed from the pulp, increasing the concentration of α -cellulose therefore decreasing the crystallinity. The lower crystallinity results in a lower strength, lower modulus and higher elongation than cotton, and lyocell, which is also a regenerated fiber with double the crystallinity of viscose, at around 80%.

1. Table. Composition of different cellulose based fibers [7]

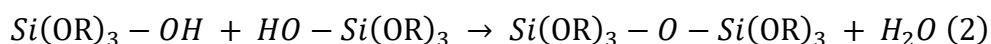
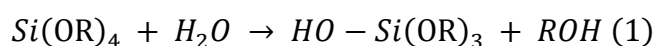
Fiber	Origin	Cellulose (wt%)	Lignin (wt%)	Hemicellulose (wt%)	Production (10 ³ t/year)
Sisal	Leaf	67.0 – 78.0	8.0 – 11.0	10.0 – 14.2	378
Cotton	Seed	82.7	-	5.7	25 000
Bamboo	Grass	26.0 – 43.0	21.0 – 31.0	30.8	30 000
Wheat	Straw	39.0 – 45.0	13.0 – 20.0	15.0 – 31.0	
Rice	Straw	41.0 – 57.0	8.0 – 19.0	33.0	
Viscose	Synthetic	100	-	-	3 500

Apart from the difference in w/w% of cellulose in the two natural cellulose fibers and regenerated cellulose fibers have another dissimilarity. This difference can be defined by the type of cellulose in the fiber. While natural fibers contain the highly crystalline cellulose-I, during the regeneration process this transforms into another form of cellulose called cellulose-II [9]. The transformation of cellulose-I into cellulose-II is an irreversible process, which means that the natural form of cellulose (cellulose-I) is actually a metastable form, while the less crystalline form (cellulose-II) is the stable variant. [10] The improved stability of cellulose-II compared to cellulose-I is attributed to the antiparallel nature of the chains, compared to parallel organization of the chains in the more crystalline form.

2.3 Cryogels

Cryogels are gels, synthesized generally by sol-gel synthesis. After the gelation a big part of the solvent (mainly alcohol or water) is replaced by a gas phase, usually air through the process of freeze drying. This drying results in a highly porous usually non-crystalline, solid material with a high specific surface area. [11] The main use cases of these porous materials can all be derived from their highly porous nature. It makes them an excellent insulator or catalyst.

Sol-gel process is a procedure, where a continuous 3D network is formed, through multiple steps of hydrolysis and condensation reactions at relatively low temperatures, usually below 100 °C. These are steps of an inorganic polymerization reaction. In the first step, the initialization, the precursor molecule reacts with the solvent molecule forming a reactive hydroxyl group on the molecule. This process can be seen in the first equation. In the next step of the polymerization, these molecules can react with each other, or with a precursor molecule in a condensation reaction with the elimination of either a water or alcohol molecule, as seen in the second equation. [12]



The initial materials are mostly metal alkoxides, like TEOS (tetraethyl- or tetramethylorthosilicate). But the Si-precursor may be Na₂SiO₃ (water glass), too. [13] During the formation of the 3D network the solvent will be encapsulated inside the pores of the gel. This property makes the replacing of solvent to a gaseous phase possible, through a drying process.

Based on the solvent used during the synthesis, the gels can be divided into two sub categories: **alcogels**, where the solvent is alcohol, and **hydrogels** with water as a solvent.

2.4 Influence of parameters of the sol-gel synthesis

The sol-gel technique though relatively simple method for the production of well-defined structures, there are numerous factors, that can be altered to modify parameters of the gel structure. [14] These factors include the quality of the precursors and solvent, the pH, the concentration of precursor solution, the catalysis, and temperature of the gelation process, the aging and drying steps. When selecting a precursor molecule with an alkyl network of higher number, the rate of hydrolysis will decrease significantly, therefore resulting in a high number of unreacted monomer molecules, capable of evaporating during the drying process.

The pH of the reaction medium can also greatly influence the quality of the gel, by modifying the ratio of the hydrolysis and condensation reactions. A more acidic ($\text{pH} < 7$) medium will shift the ratio towards the hydrolysis (the reaction is more favorable thermodynamically), resulting in a higher concentration of hydrolyzed monomer molecules. While in the case of a basic environment, the condensation will be thermodynamically more favorable, resulting in a negligible concentration of hydrolyzed monomer molecules. This property of the synthesis actually proves to be useful in a few scenarios, like in the case of TEOS, the hydrolysis reaction is less prominent than the condensation, due to the low electropositive nature of silicon, by changing the pH of the system to a more acidic solution, the balance of the reactions can be restored [15].

The last parameter of the synthesis that can be effectively changed during the reaction to get a desired structure, is the ratio of precursor and solvent in the initial solution. By increasing the solvent concentration, the concentration of produced oligomers can be significantly reduced, while increasing the SiO_2 chains. Increasing the solvent concentration compared to the precursor can also increase the time of gelation and therefore the average pore size of the dry gel. On the other hand by decreasing the solvent concentration we can achieve a much faster gelation, with a smaller average pore size.

After the gelation there are ways to alter the final gel structure. The first step may be the aging process, which is a further treatment usually at temperature of gelation. Aging is the result of further hydrolysis and condensation reactions even after the formation of gel, since these processes are not finalized during the main gelation. The second step is the drying process. [16]

2.5 Drying process

The aim of the drying process is to remove of the main part of solvent. The drying processes may be atmospheric drying to produce xerogels; freeze drying for cryogels; and supercritical drying resulting in aerogels. The aerogels can keep the 3D structure of “wet” gel resulting in a porosity of around 80-95%. [17] The xerogels have a more compact structure, with their porosity of 10-50 %. Freeze drying provides also a high porosity 40 – 80 % for the materials. [18] The difference from the aerogel, the aerogels can be characterized by nanopore systems, while the cryogel is typically macroporous. But monolith systems cannot be obtained by cryogenic processes. Freeze drying also known as lyophilisation is a low temperature dehydration/desolvation process. The pore liquid is frozen and the resulting solid/ice is sublimated under vacuum, leading to formation of porous structures. Pore size, pore volume and pore morphology are dependent on variables such as freeze temperature, freezing rate, solution concentration, nature of solvent and solute, and the control of the freeze direction. Freeze drying consists of three main stages. At the first stage, the gel should be frozen. One of the most important cryogenic parameter is the rate of freezing. With higher freezing rate, the cryogels have a homogeneous distribution of pores with smaller average diameter. While in the case of a slower rate, the formation of ice-cores is slower, therefore bigger ice crystals are forming, resulting in a higher average diameter of pores. [19] The second stage of freeze drying is the main drying step, carried off in vacuum. During this stage, the pressure of the chamber is lowered below the triple point of the solvent of the gel. Once this triple point is reached, the solvent sublimates as vapor. The last stage of the process is the secondary drying, which is required, since during the main drying step some residual solvent is left in the system. This step is usually done at a lower vacuum. [20]

2.6 Solving the problems of cryogels

Main problem is the cracking of the structure due to the frozen solvent crystals, resulting in smaller fragments instead of a continuous monolith structure. To solve this, multiple answers were already proposed in literature with different degree of success [21-22]. These solutions may be increasing the density of the gel by growing the concentration of starting solution, which could result in a smaller porosity, therefore reducing its insulator capability. That is not so efficient solution. Coating the gels by a polymeric layer may be also proposed to decrease

rigidity of the dry gel. The best method is the application of the cryogel particles as a dispersed reinforcing material in a composite system.

2.7 Composite materials

A composite material can be defined as a system consisting of at least two macroscopically distinguishable phases, that are insoluble in each other, and the main interaction between the phases comes in the form of secondary bonds. The continuous phase of the system is given by the matrix which is strengthened by a dispersed reinforcement phase. The reinforcing second phase may be fibers, particles, or even layers. The form of reinforcement phase is usually the determining factor in categorizing these systems, therefore four main groups of composite materials can be defined: these are fiber-reinforced, particle-reinforced, layered composites and the mixture of these three in different ratios. Composite materials can also be characterized by their matrix material. Based on the matrix there can be metal or non-metal composites [23]. The goal of composite formation is to keep the advantageous properties of the original materials, while increasing these, already present, physical properties. In a lot of situations a completely new property can appear, which was not present in any of the original materials, these properties are called synergic properties.

3. GOALS

The goal of this study is the development of new, low-cost synthesis route for biodegradable thermal insulation layers. Nowadays, a very important task is to evolve a thermal insulation composite layer for coating of geometry-free surfaces. Moreover, the aim of this research is to prepare biodegradable layers regarding the importance of the environmental protection. The cellulose fiber and textile was aimed to use as matrix component in the composite systems. The cellulose is a biodegradable and biocompatible materials. Moreover, the cellulose has the highest thermal insulation ability from the commercial polymers. Silica cryogel was selected for the reinforcing phase. The silica cryogel can be characterized by excellent resistance against the heat and chemical impacts. The sol-gel method was applied as synthesis of composite layer. In this task, the preparation conditions, the ratio of matrix and dispersed phase were aimed to optimize. The task in this part of research covered the solution of the connection between two phases.

Beside the preparation, the other very important aim was to investigate the composite structure. Scanning electron microscopy was applied, to investigate the general structure, morphology and homogeneity of the composite systems, while infrared spectroscopy (FT-IR) was utilized to determine the bond structure of the composite systems. The final products of our synthesis were characterized by heat conductivity measurements.

4. EXPERIMENTAL

In this thesis, the synthesis of cryogels was carried out with varying precursors, namely sodium silicate solution and TEOS as Si-precursor, in vastly different reaction conditions. Recipes developed previously in the Sol-gel Laboratory of the institution, also used in my BSc thesis, were used as a basis for the new synthesis methods discussed here. In the case of sodium silicate based gels, the influence of pH on the final gel was studied, along with the type of catalyst used to achieve gelation. While in the case of TEOS based cryogels, the effect of precursor solvent ratio was studied along with effect of different additives to the system before gelation.

4.1 Methods of examination

In present thesis, two main examination methods were used to characterize the produced materials. Scanning electron microscopy was used to provide a general look into the structure of the cryogels, and a mean to determine its average pore size or average porosity in percentage compared to the gel structure. Meanwhile, infrared spectroscopy was used to get an idea about new interactions between the components of the composite systems, by providing a view of their bond structure.

4.1.1 Infrared microcopy (FT-IR)

Infrared spectroscopy is a type of vibrational spectroscopy, which is used mostly for the determination of the existence of specific functional group in a molecule. The sample is irradiated by a light source in the infrared range, and absorbance is measured in its function. The result of this measurement is the infrared spectra, which contains peaks at specific wave lengths, highly dependent on the functional groups, and bonds. The above-mentioned absorbance of the irradiating light can be given by a simple equation of:

$$A = \log\left(\frac{I_0}{I}\right)$$

Where A is the absorbance, I_0 is the intensity of the original, irradiating light, and I is the intensity of the light after interacting with the sample. [25]

4.1.2 Scanning electron microscopy (SEM)

As the name suggests electron microscopy devices are similar in function to a standard imaging microscope, but instead of light used for irradiating the sample, creating a magnified image a beam of accelerated electrons is used as a source of irradiation.

When the electron beam reaches the surface of the sample, it can interact with the sample elastically or inelastically. Elastic interactions happen, when the incoming electron collides either with the atom core of the sample, or with an electron of comparable energy located on an

outer electron shell. Causing diversion of the incoming electron from its original direction, with minimal energy loss. On the other hand, inelastic interaction is also possible between the electrons and the surface, when an incoming electron gives significant energy to the atoms of the sample. This increase in energy ionizes the atom of the sample, resulting in the ejection of a loosely bonded electron, called secondary electron. [26] Due to relatively low energy of these secondary electrons, their travel distance is low, making their detection, with good resolution relatively simple. The detection is done by first converting the energy of the detected electrons into photons with a scintillator. Through a plexiglass, or quartz windows these photons are directed towards a photon-multiplier, where their energy is converted back to electrons. This detection method enables mapping of the topography of a sample. [27]

The other main method of detection, is based on the detection of back scattering electrons with more than 50 eV energy, scattered during the interaction between the electron beam and sample. This detection method provides both a topographical view of the surface of a sample and its general chemical composition.

For present thesis, the FEI Quanta FEG microscope was used to prepare the micrographs. Specifically its Everhard-Thornley secondary electron detector (ETD), low vacuum secondary electron detector (LVSED) and low voltage, high contrast detector (vCD) was used. The sample were fixed onto the sample holder by a two-sided graphite tape, without any conductive coating on the sample.

4.2 Materials

Table 1. Containing all materials used in the research with their respective purity and w/w%

Material	W/w%	Manufacturer	Grade of purity
TEOS	100%	Sigma-Aldrich	98%
Sodium silicate solution	36.7 %	VWR	Technological purity
Urea	100 %	VWR	Technological purity
Ethyl-alcohol	99.8 %	Lachner	ISO General reagent purity
HEC	100 %	Molar-chem. kft	99.9 %
N-propanol	100 %	VWR	Analitic purity
HCl	37%	VWR	Analitic purity
Cotton	90%	-	90% cellulose, 10% other
Viscose	100%	-	100% cellulose
HNO ³	65.6 %	VWR	Analitic purity
Perchloric acid	60%	VWR	Analitic purity

4.3 Sodium silicate based cryogels

4.3.1 Investigation of pH dependence

Original recipe, pH = 9

The 36.7 w/w% water glass solution (sodium silicate) is diluted in a beaker to achieve a solution of 10 w/w%. During continuous stirring at room temperature, HNO_3 with a concentration of 2 mol/dm³ is added to the solution, drop by drop, until the solution reaches its gelation point. At this point the stirring is stopped to preserve the forming 3D network's integrity. The nitric acid acts as an acidic catalyst, during the reaction, lowering the pH of the water glass solution (original pH = 12). After gelation the gels are kept at room temperature for the aging process, for 2-3 days.

The resulting gels are frozen in liquid nitrogen for 5 to 10 minutes, and the solvent crystals are sublimated in a freeze-dryer for 72 hours in a pressure of 0.001 mbar.

pH = 11

For the next synthesis, the goal was to achieve gelation with the addition of the least possible acidic catalyst. Similarly to the previous synthesis, a diluted water glass solution was prepared with a w/w% of 10 % from the original solution (36.7%) in a beaker. Nitric acid with a concentration of 2 mol/dm³ was added to the prepared solution, a few drops at a time, and the solution was left, for gelation. After the final drop of nitric acid, the pH of the system reached 11 from the original pH of 12, and the gelation took for 20 hours to complete.

The gel was then aged for 2-3 days, and was freeze-dried with the same method, in the same environment as before with liquid nitrogen.

pH = 3

Similarly to the previous techniques, a 10 w% sodium silicate solution was prepared by dilution of the original sodium silicate solution, with a w/w% of 36.7% with distilled water in a beaker. In the original experiment (pH=9), adding the acidic catalyst drop-wise resulted in an instant gelation at a pH value of 9, so this time the nitric acid of 2 mol/dm³ concentration was added to the system all at once. The addition of the catalyst shifted the pH value to 3, but resulted in a drawn out gelation time, compared to the original recipe. The gelation took for 21 hours, and the aging process at room temperature took for total of 2-3 days. After which the gel was frozen with liquid nitrogen and freeze-dried for 72 hours in a pressure of 0.001 mbar.

pH = 1

After preparing cryogels with pH value of 3, it was tested if further decrease of pH is possible through the previous synthesis process. So the amount of acidic catalyst added to the system

was adjusted to reach pH=1 in the solution. The first experiment, though achieved the correct pH value, resulted in no gelation of the system after multiple days of waiting, so the procedure was adjusted. In the new experiment, the first part of the 2 M nitric acid was added to the system drop-wise, to almost reach the point of gelation, and then the pH of the system was adjusted, to achieve a pH of 1. The second trial was successful, but the gelation still took quite some time (multiple days), due to the increase of distilled water added to the solution through the increase of nitric acid (dilution of the system). Thus, a new experiment was conducted, with a new nitric acid solution, which had a concentration of 4 mol/dm³. This resulted in a much shorter gelation time of 6 hours. The gel was frozen in liquid nitrogen for 5-10 minutes, and then freeze-dried for 72 hours at a pressure of 0.001 mbar.

Summary of pH effect

The gels synthesized in this chapter used the same 10 w/w% sodium silicate as the precursor of the cryogels, with distinct acidic catalyst to precursor ratios. The pH of the environment showed a high influence on gelation time. The quantities used for the synthesis can be found in Table 2 below. In all experiments the 10 w/w% water glass solution was prepared by adding 3.5 mol distilled water to 0.19 mol 36.7 % sodium silicate solution.

Table 2. Quantities used to synthesize gels with different pH values

pH value	HNO ₃ solution (acidic catalyst)			gelation time
	conc. (mol/dm ³)	quantity / mol	precursor : HNO ₃ molar ratio	
9	2	0.036	5.277 : 1	instant
11	2	0.016	11.875 : 1	20 hours
3	2	0.06	3.166 : 1	21 hours
1	4	0.12	1.583 : 1	6 hours

4.3.2 Influence of the type of acidic catalyst used

Nitric acid was used in the original recipe, as well as the experiments investigating the effect of pH on the gel. Apart from HNO₃, two other catalysts, hydrochloric acid and perchloric acid, were tested in this research. The preparation of these gels is described below.

Perchloric acid

For the synthesis the original recipe was used, as described in chapter 4.3.1, pH = 9. The water glass solution was diluted to achieve a w/w% of 10 % (original had a w/w% of 36.7%), in a beaker. During continuous stirring, perchloric acid was added to the solution drop-wise. When the system reached a pH value of between 8-9, a precipitation was observable at some parts of

the system, but the gelation of the solution did not happen. In the next experiment smaller amount of perchloric acid was used, to avoid precipitation in the system, but even after 5-6 days of waiting the gelation did not carry out. Due to the lack of gelation, no cryogels were formed using this method of acidic catalyst.

Hydrochloric acid

In this, next experiment the possibility of using HCl as an acidic catalyst in place of nitric acid was investigated. For this the water glass solution was diluted to as solution similar to the previous experiment, with a w/w% of 10%. This time a hydrochloric acid solution with a concentration of 2 mol/dm^3 was poured to the solution drop-wise. When the water glass solution reached a pH of 8 the gelation of the system happened instantly. After 2-3 days of aging, the gel was frozen in liquid nitrogen and put into the freeze dryer for 72 hours.

Summary of acidic catalyst's effect

The effect of the type of acidic catalyst showed a lack of results due to the failed attempt to synthesize gels from perchloric acid. Used quantities for the sample are summarized in Table 3. In all methods, the precursor was a 10 w/w% sodium silicate prepared by adding 3.5 mol distilled water to 0.19 mol 36.7 w/w% sodium silicate solution.

Table 3. Quantities used for determining the effect of different type of acidic catalyst for the sol-gel process

Acidic catalyst				Gelation
type	Conc. (mol/dm^3)	Quantity / mol	Precursor : HNO_3 molar ratio	
HNO_3	2	0.036	5.277 : 1	+
HCl	2	0.036	5.277 : 1	+
Perchloric acid	2	0.036	5.277 : 1	precipitations

4.3.3 No acidic catalyst – ion exchange

During this research the possibility of gelation without acidic catalyst was also explored. The idea behind the process was to lower the pH of the solution to a similar value to the original recipe. This method was carried out using a cation exchange resin, which is capable of replacing the Na^+ ions in the water glass solution for H^+ ions. The process was carried out multiple times, each time pouring the sodium silicate solution through different height of ion exchange resins. Both experiments used a 10 w/w% sodium silicate solution prepared by adding 65.26 g distilled water to 23.45 g 36.7 w/w% water glass solution.

10 cm tall cation exchange resin

Similarly to the previous experiments, the ion exchange was also done on a diluted sodium silicate solution, so a solution of water glass, with 10 w/w % was prepared. The solution was poured into an ion exchange column containing cation exchange resin, previously activated by oozing 10 w/w% HCl through it. The column was set up to form a droplet every 1-2 seconds, until the whole solution dropped through the system. Finally, all leftover solution on the resin was washed into the beaker by distilled water. This way the pH of the system reached six, and the gelation happened in 20 hours.

10 cm + 15 cm tall cation exchange resin

In the second experiment, the effect of a longer ion exchange column on the pH and gelation time was investigated. Since the column could only house a max resin height of 15 cm, the solution was first poured onto the resin with a height of 10 cm, with the flow rate set at around 1 drops per 1-2 seconds. After the first ion exchange step, the process was repeated, but this time with a column height of 15 cm. This way the solution flown through a 25 cm cation exchange resin, but neither the pH of the end solution or the gelation time changed from the previous experiment.

4.4 Tetraethyl orthosilicate based cryogels

During my BSc thesis, TEOS based cryogels were neglected due to the relatively high gelation time during the sol-gel synthesis. Moreover, TEOS has a much higher cost compared to water glass and the relatively lower porosity of its cryogels. During present thesis, possible solutions for these problems were explored.

4.4.1 Original recipe

For the process tetraethyl orthosilicate is dissolved in ethyl alcohol, and nitric acid with a concentration of 2 mol/dm³, is used as a catalyst of the sol-gel synthesis. The catalyst was added to the alcoholic solution of TEOS during stirring. The system was heated to 80 °C, with a continuous stirring for an additional hour, with a reflux cooler installed onto the spherical flask. At the end of the hour mark the stirring is stopped, and the solution is heated until gelation. The average time of gelation based on multiple experiments is 72 hours.

The gels were then frozen with liquid nitrogen and freeze-dried for 72 hours under vacuum. The final cryogels are glassy pieces, with high shrinkage compared to the wet gels, and water glass based solutions.

4.4.2 Modified TEOS – ethanol ratio

In chapter 4.4.1 the molar ratio of TEOS : ethanol : HNO₃ was 1 : 10 : 1. The same experiment, with the same procedure was carried out with a modified ratio of TEOS : ethanol : HNO₃ at 1 : 4 : 3. This time, after stirring the solution with a continuous heating at 80 °C, the gelation of the system occurs in a much shorter timeframe, one hour of heat treatment without stirring. This way, the original time requirement of 72 hours could be reduced to a much lower time requirement of 2 hours from start to finish. After an aging process of 2-3 days the gels were freeze-dried to form porous cryogels. Based on initial experiences the gel showed a similar level of shrinkage as the original production method.

4.4.3 Water – ethanol solvent mixtures

During my BSc thesis it was found that cryogels based on TEOS have a significantly lower porosity, when compared to water glass systems. For the improvement of its porosity the sol-gel process described in the previous two chapters was slightly altered. In this experiment after dropping the acidic catalyst (2M nitric acid) to the ethanol TEOS solution, with a continuous stirring at a temperature of 80 °C for one hour, the solution was vacuum distilled to half volume. The missing solvent was replaced by distilled water (to match original volume), and the system was kept at room temperature until gelation which took place one in one hour.

After 2-3 days of aging the gels were freeze-dried in the same conditions as before. The cryogels showed a lower level of shrinkage than the original synthesis method, which can be attributed to the water content. Thus, the porosity should be increased.

4.4.4 Additives

The effect of two additives was investigated on the procedure described in the 4.4.2 paragraph. The two additives were NH₃ and citric acid, where the effect of NH₃ was also tested without the addition of acidic catalyst to the system. The addition of propylene-oxide was also investigated during the research.

NH₃

As previously mentioned the influence of NH₃ as additive was tested in two distinct cases. In the first experiment the effect of NH₃ was tested. The solution was prepared in the same way as in the 4.4.2 procedure, but after the addition of nitric acid, 2M NH₃ was also added to the solution drop-wise. The system did not show any signs of gelation, but precipitations were forming at parts of the solution.

To stop precipitation in the system, the same experiment was repeated, but without the addition of nitric acid to the system. Once again the gelation of the system did not occur, but the addition of 2M NH₃ to the solution resulted in an immediate formation of sol, which was liophylized, in the same conditions as the other experiments, to get a white powder.

Citric acid

Citric acid was also tried as an additive in the synthesis described in 4.4.2. Right after the addition of HNO₃, powdered citric acid was added to the system, with continuous heat treatment at 80 °C. The resulting gels were freeze-dried to form cryogels. The dried gels showed a high level of shrinkage, and a slight yellow tint compared to the wet gels.

Propylene-oxide

The last additive tried for the sol-gel synthesis was propylene oxide, added to the system in place of an acidic catalyst. Propylene oxide is a gelation agent. Thus, it was surprising, that the gelation time significantly increased, with 120 hours. The typical result of the use of propylene oxide is the reduction of gel time to 1-2 hours. After gelation, the gels were freeze-dried in the same way as before. Final cryogels showed higher level of shrinkage than any other sample in the series.

4.4.5 Summary of the preparation conditions' effect on cryogels derived from TEOS

Table 4. Materials used for the synthesis of TEOS based cryogels

solvent			catalyst		additive	
type	quantity / mol	ratio to TEOS	type	quantity / mol	type	quantity / mol
alcoholic solution of TEOS	0.2	1 : 10	HNO ₃	$7.2 \cdot 10^{-3}$	-	-
	0.08	1 : 4	HNO ₃	$7.2 \cdot 10^{-3}$	-	-
	0.08	1 : 4	HNO ₃	$7.2 \cdot 10^{-3}$	citric acid	0.002
	0.08	1 : 4	-	-	NH ₃	0.02
	0.08	1 : 4	-	-	propylene-oxide	0.057
water – alcohol	0.08	1 : 4	HNO ₃	$7.2 \cdot 10^{-3}$	-	-

4.5 Establishing composite systems

In order to improve the physical properties, to produce a continuous thermal insulation layer, the main aim was to form composite materials. The cellulose fibers or textile provide the matrix of the composites by connecting with the cryogel species. Here our goal was to determine the best possible way to establish composite materials between cellulose fibers and cryogels, and

to decide whether TEOS or water glass based cryogels have better interactions with the matrix of the composite (cellulose). For the improvement of linkage between the matrix and dispersed phase, additives were also used during the synthesis, these included hydroxyethyl cellulose (HEC), and a solvent mixture of NaOH in different concentrations ranging from 2M NaOH, 2M carbamide to 5M NaOH and 5M carbamide. HEC is capable of reacting with hydroxy groups of the silica gels through their own OH groups, while the solvent mixture is capable of partially dissolving the fibers.

4.5.1 Cryogels + HEC

For a more homogeneous distribution of reinforcement phase, the cryogels were first milled and sieved into units smaller than 250 μm . Milled cryogels were added to a viscous solution of HEC dissolved in distilled water. During continuous stirring, the cellulose fibers, cut into smaller pieces than 1 cm, were added to the solution. The result was a white sticky paste. The experiment was carried out for both the water glass and TEOS based cryogels. Used quantities can be found in the table below.

Table 5. Containing quantities used during the formation of composite materials with only HEC as an additive

Cryogel type	Cryogel / g	HEC / g	Distilled water / ml	Viscose fiber / g
TEOS(original)	2.0	0.4	10	0.4
Water glass(pH=9)	2.0	0.4	10	0.4

4.5.2 Application of cotton in composite systems (with NaOH, carbamide and HEC)

The first step of the synthesis is the preparation of solvent mixture used for partially dissolving the cotton fibers, to improve reactivity between the surface of cotton and cryogel. The solvent was prepared by dissolving the corresponding quantities of both solid NaOH and carbamide in distilled water. The first mixture had a NaOH, and carbamide concentration of 2 mol/dm³, which was increased for both materials in the subsequent experiments until the solvent mixture had a concentration of 5 mol/dm³ for both components (The composition of each experiment is summarized in Table 5.). The cotton was then cut into fibers with a smaller average length than 1 cm, and submerged in the previously prepared solvent mixture for 30 minutes, this results in the swelling of cellulose fibers. During continuous stirring with a KPG mechanical mixer, the cryogel, milled and sieved under 250 μm , was added to the system. Both main cryogel types

(TEOS and sodium silicate based) were tried in the composite materials, but due to the difference in average porosity between the two, water glass based cryogels were prioritized. The system was further stirred at a temperature of 65 °C until a mostly homogeneous solution was achieved, with an equal distribution of fibers. At the end of the process the system was vacuum distilled until a spreadable paste like consistency.

Table 6. Containing all experiments done with cotton fibers as the matrix of the composite

Cryogel (smaller than 250 μm)		Solvent mixture concentration for:		HEC / g	fiber
type	Quantity / g	NaOH (mol/dm ³)	Urea (mol/dm ³)		
TEOS (original)	2.0	2	2	-	0.4 g Cotton fiber cut into an average length of below 1 cm
		5	2	-	
		2	2	0.4	
5		2	0.4		
Sodium silicate (Original procedure, pH=9)		2	2	-	
		2	2	0.4	
	5	5	-		
	5	5	0.4		

The experiments showed a high time requirement of around 40-50 hours for the homogenization of fibers, and even then, a completely, macroscopically homogeneous system was never achieved. The addition of HEC improved the time required for the same level of homogeneity as before, but it was still far from a homogeneous system. With an increase in NaOH and carbamide concentration the system required around 20 hours of stirring for a better homogeneity than the previous experiments but still showed parts of cellulose fibers stuck together in big chunks, which did not improve much by the addition of HEC. Due to this reason the usage of cotton fibers were dismissed, and our attention was refocused to pure cellulose fibers.

4.5.3 Cryogels + NaOH – carbamide solvent + pure cellulose fibers

The process described in 4.5.2 was repeated with pure cellulose fibers in the place of the cotton fibers, Apart from the cellulose content, the type of cellulose was also considered in the selection, since this type of cellulose contains a cellulose allotrope with much lower crystallinity, the cellulose-II, resulting in higher reactivity compared to the more crystalline

cellulose-I version. Since the initial experiments showed a much higher homogeneity compared to the cotton variant, this was selected as the main method of synthesis. The experiments based on this process can be found in Table 7.

Table 7. Containing all experiments done with regenerated pure cellulose fibers as the matrix of the composites

Cryogel (smaller than 250 μm)		Solvent mixture concentration for:		HEC / g	fiber
type	Quantity / g	NaOH (mol/dm^3)	Urea (mol/dm^3)		
TEOS (original)	2.0	2	2	-	0.4 g pure cellulose fiber cut into length shorter than 1 cm
		2	2	0.4	
		5	2	-	
sodium silicate based cryogel synthesized by the original process (pH=9)		5	2	0.4	
		2	2	-	
		2	2	0.4	
		5	5	-	
sodium silicate cryogel pH=1		5	5	0.4	
		5	5	-	

The experiments showed that the replacement of cotton fibers, with pure cellulose fibers not only improved the general homogeneity of the system by a large margin, it also significantly reduced the time requirement, for achieving this state. In the case of the first system with 2-2 M concentration of both NaOH and carbamide the time of preparation was reduced from 50 hours to 25 hours in the case of cellulose-2. The synthesis time proved to be further reducible by increasing the concentration of both sodium-hydroxide and urea to 5M respectively. This way the time requirement for the procedure was only 16 hours. The addition of HEC, although did not change the homogenization time significantly, proved to be important for an improved reaction between the phases of the composite.

Based on the result of the scanning electron microscopy measurements of all cryogel samples, sodium silicate based cryogels were selected where the pH of the system before the gelation was 1.

4.5.4 cryogel and textile composite

The usage of textile, as a reinforcement phase, was also explored during the research. Textile is a material consisting of 100% cellulose. The main goal was to reinforce the cryogels, before the freeze-drying process during the synthesis, and carry off the liophylization with the textile sheet,

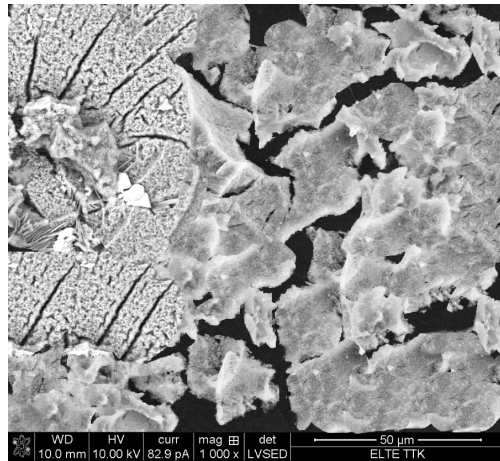
to keep a monolith structure and keep the loose porous structure of the cryogel. Since the synthesis of the pH=1, sodium silicate based cryogel required a couple of hours before gelation this was selected as the gel of the matrix. Based on the previous experiments, before the addition of the textile sheet to the solution, it was treated with a NaOH – carbamide solvent mixture. Both 2-2 M mixture and 5-5 M mixture was tried, but in the case of the more concentrated solution the shrinkage of the sheet was so significant that it was discarded. After treatment, the sheet was added to the solution of water glass, and the gelation happened in 10 hours. The gels were frozen with liquid nitrogen and dried under vacuum by freeze drying. The resulting cryogel showed a monolithic structure.

5. RESULTS

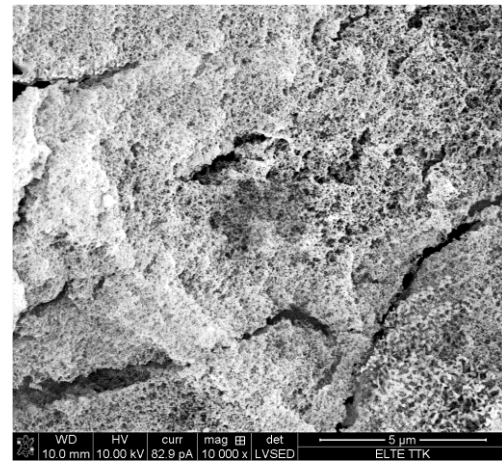
5.1 influence of pH on the cryogel structure (sodium silicate)

To determine the effect of gelation pH on the structure of cryogels, the samples prepared in chapter 4.3.1 were investigated using scanning electron microscopy. The recorded micrographs were used, in determining an average porosity of the cryogels, and finding a size distribution of pores in the dry gels, as well as the homogeneity of the samples.

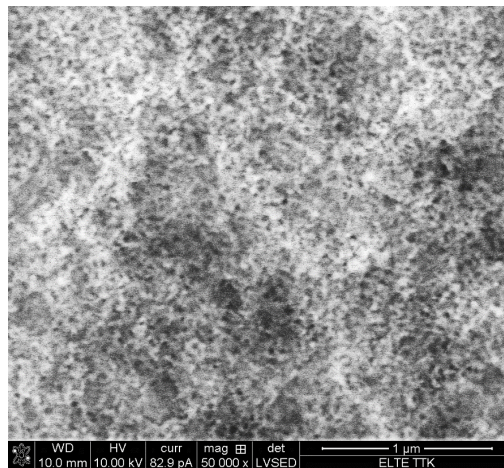
Original recipe, pH = 9



1 000x magnifications



10 000x magnifications



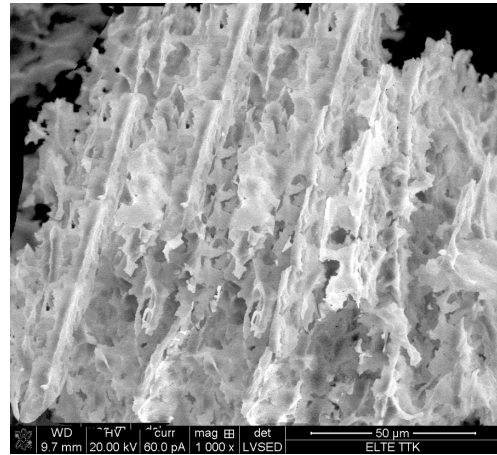
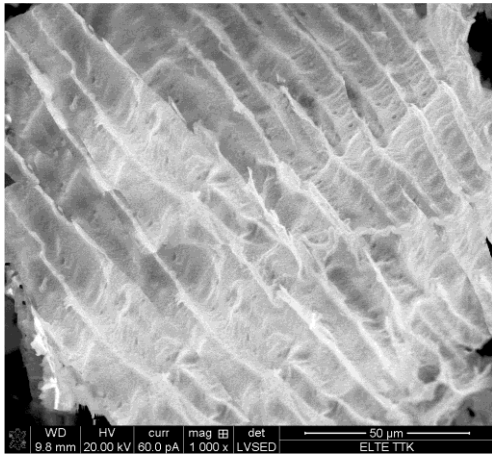
50 000x magnifications

Figure 1. SEM recordings of silica cryogels (water glass, pH 9), with different magnifications

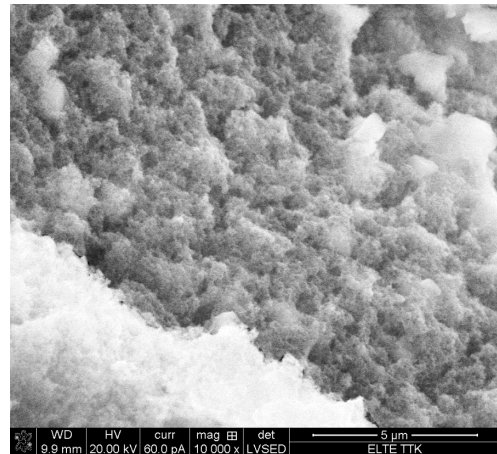
The scanning electron microscopy images taken from the samples synthesized by the original process (pH = 9), from water glass solution, showed a high level of ordered, aggregated structure with a homogeneous distribution of pores. Based on the images, the macropores are missing from the structure, with most pores ranging from 20 nm to 100 nm in diameter, and an

average pore size of 40 nm, determined from the 50 000x magnifications. The porosity of the gel varied between 55 and 60 % with an average of 57%.

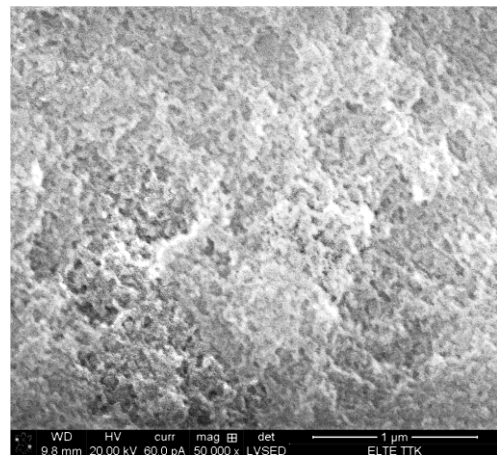
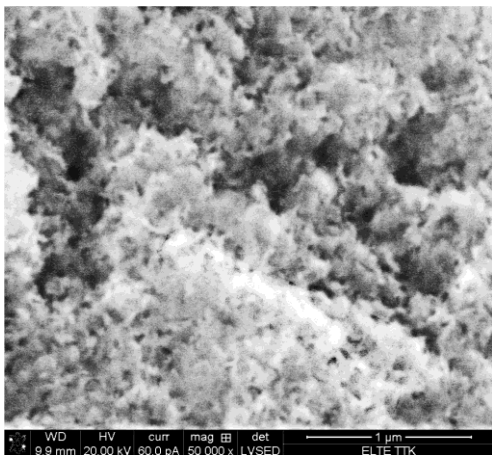
pH = 11 cryogels



1 000x magnifications



10 000x magnifications



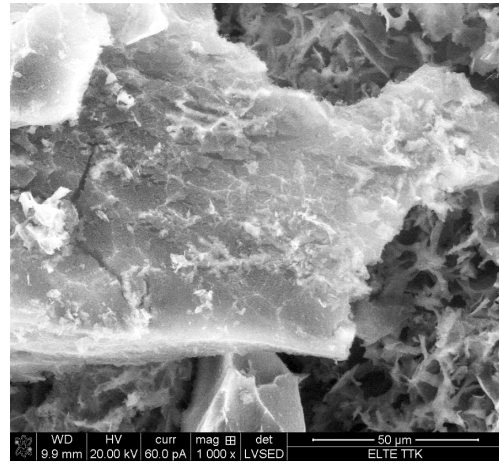
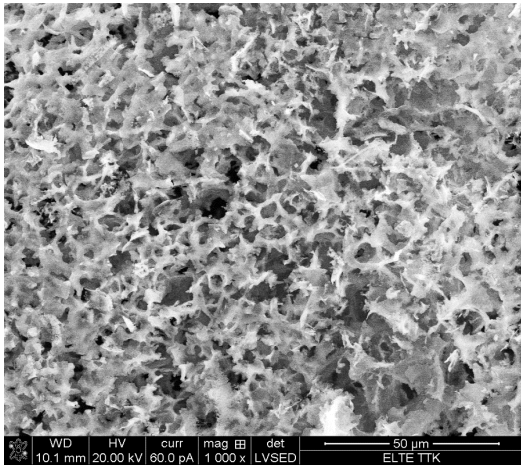
50 000x magnifications

Figure 2. SEM images of silica cryogels (water glass, pH 11), with different magnifications

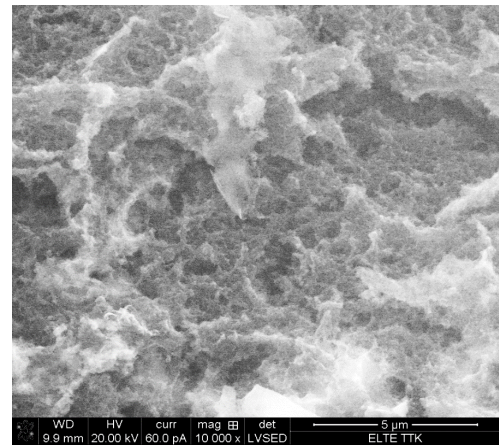
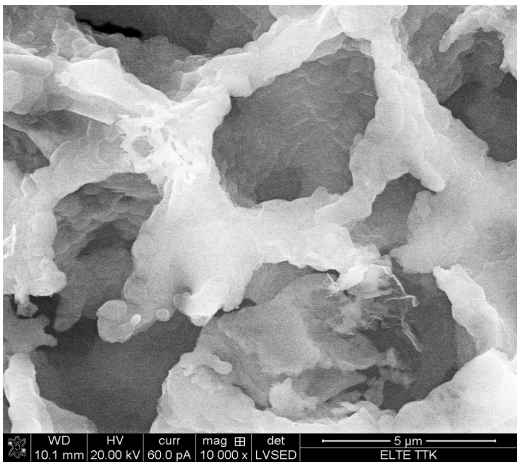
The sample shows a mostly homogeneous aggregated structure without compact parts. The gel has a hierarchical structure with bigger macropores, columns or partially broken anisotropic pores all being present, based on the 1000 times magnifications. The average size of macropores is between 20 and 40 μm , while the diameter of the columns ranges from 8 μm to 12 μm (1000x). Due to its hierarchical structure, nanopores are also observable in the wall of the macropores and columns, with an average diameter of 20-200 nm and typical size of 25-80 nm, based on the images of 50 000x magnifications. The porosity of the cryogel was 61.5 % at average, which is the lowest in the series.

pH = 3 cryogels

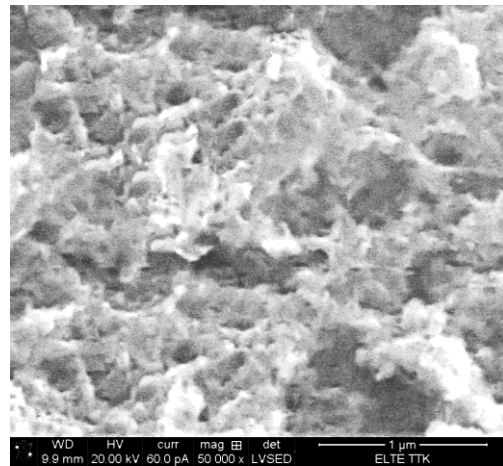
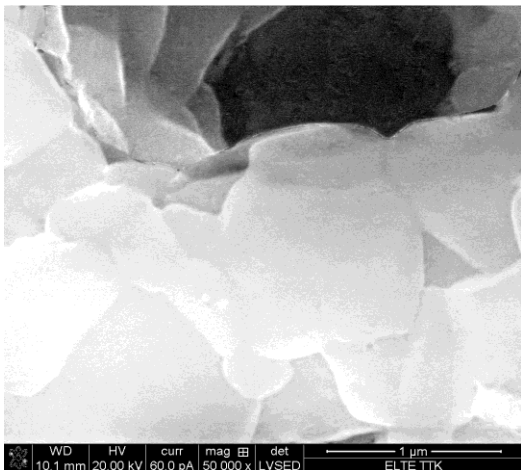
The cryogel shows a relatively high level of inhomogeneity, with higher average porosity than the previous sample (pH 11), at 62%. The inhomogeneity of the sample manifests itself in the presence of both porous and compact parts as seen on both the 1000x and 50000x magnifications. The pore size varies in a wide range with nanopores at 20 nm to macropores with a maximum diameter of 5 μm . Based on the images with lower magnifications (1000x) 3-5 μm pores are dominating the structure, with smaller pores in the range of 600-2000 nm scattered around, while on bigger magnification images, 40-300 nm pores amount to the majority of the porosity. This property indicates a hierarchical pore structure.



1 000x magnifications



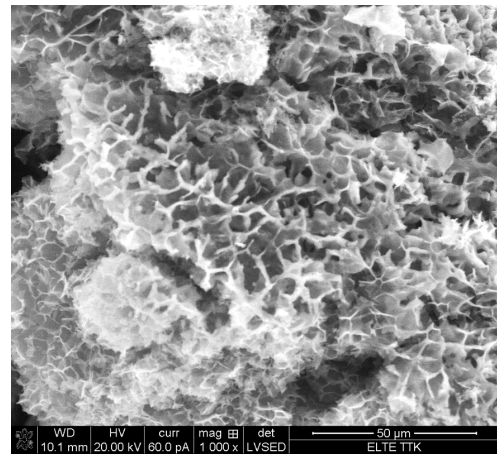
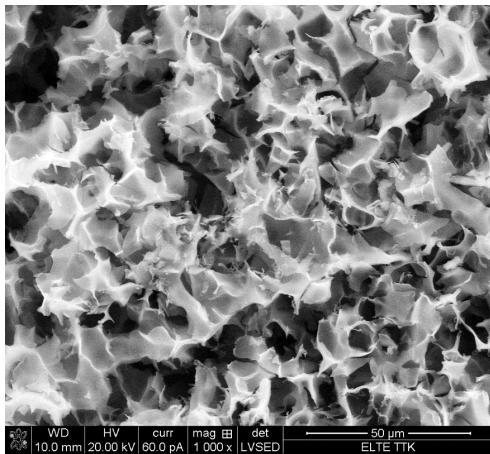
10 000x magnifications



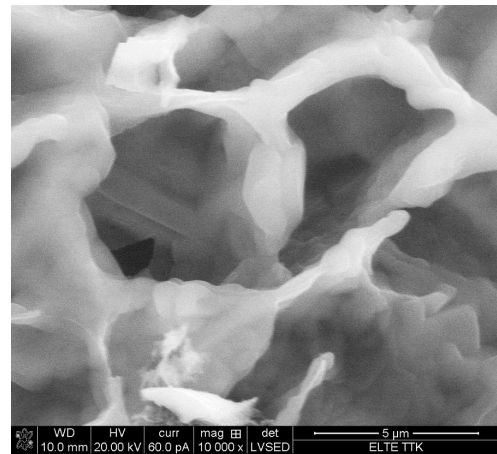
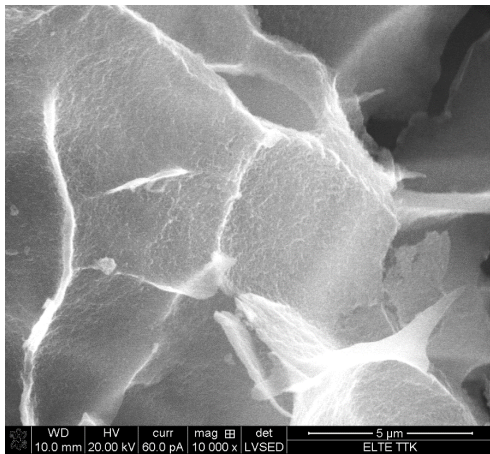
50 000x magnifications

Figure 3. SEM images of silica cryogels (water glass, pH 3), with different magnifications

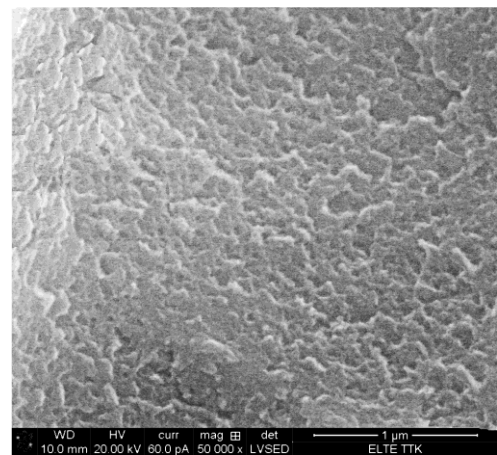
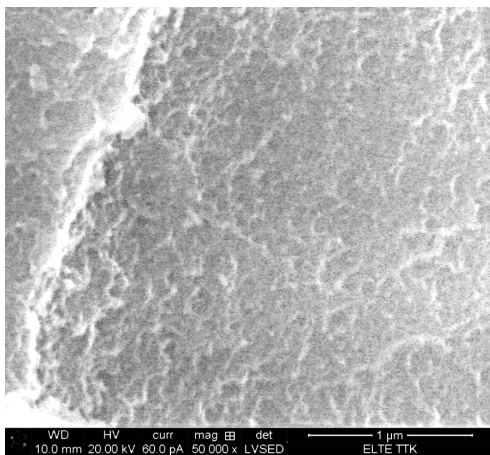
pH = 1 cryogels



1 000x magnifications



10 000x magnifications



50 000x magnifications

Figure 4: Showing all SEM micrographs recorded from the pH=1 sample, with different magnifications

The cryogel shows a highly porous, homogeneous structure, with the highest porosity of the series. Based on the images with 1000x magnification, the pores are isotropic, with a loose structure and thin walls. As isotropic pores, the size distribution is quite narrow, most of the macropores being in the range of 3-7 μm , with a wall thickness of around 600 nm on average. As the magnification increases (10 000x, 50 000x) nanopores with an 60 nm average \varnothing , are revealed, indicating a hierarchical pore structure. The average porosity of the cryogel is 66%.

Summary of pH effect by SEM investigation

The experiment showed a big variation in general structure, depending on the pH of the gelation. It greatly influenced the homogeneity, average pore size and porosity of the sample. Since the sample with a pH value of 1 showed the most homogeneous structure, with the highest porosity, and narrow distribution of both macro- and nanopores it was selected as the best cryogel. The results are concluded in the table below. Change of porosity in the function of solution pH can be seen on the Figure 5.

Table 8. Summary of physical properties determined from the SEM micrographs

Precursor	pH	Porosity/ %	Pore size / nm		Homogeneity
			macropores	nanopores	
10 w/w% sodium silicate solution	11	61.5	20000 - 40000	25 - 80	mostly homogeneous
	9	57	-	20 -100	mostly homogeneous
	3	62	3000 - 10000	40 - 300	inhomogeneous
	1	66	3000 - 7000	20 - 60	homogeneous

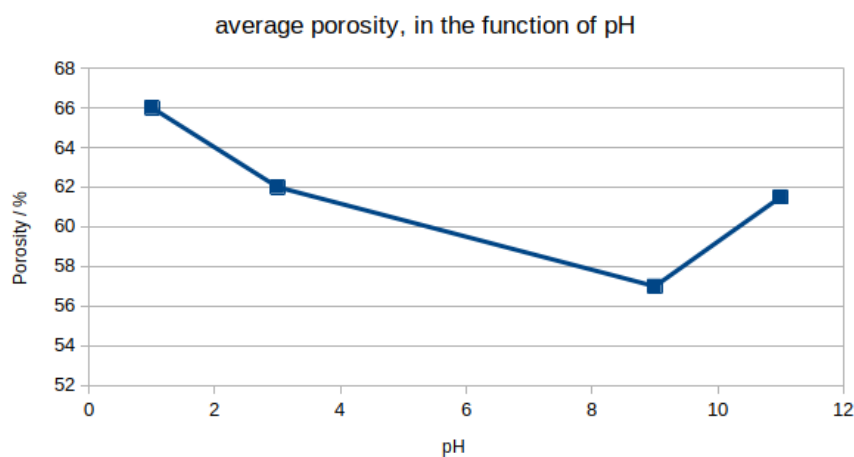
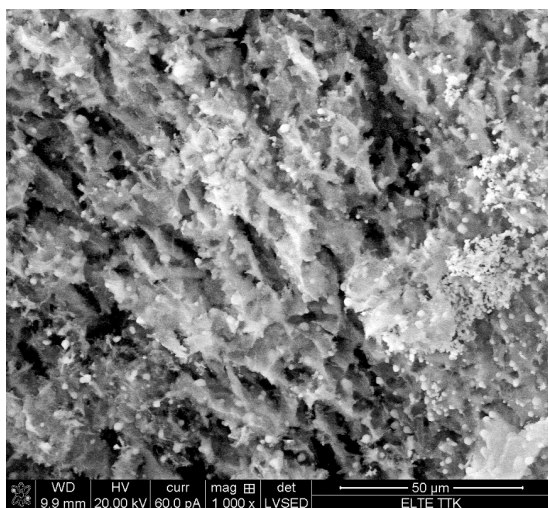


Figure 5. The change of average porosity of the sample in the function of solution pH during the sol-gel synthesis

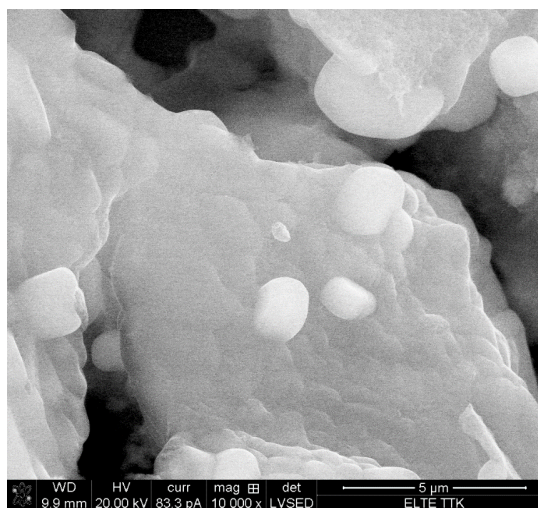
5.2 Influence of catalysis method on cryogel structures

As described in chapter 4.3, the effect of different catalysis methods, on the cryogel morphology was also investigated. Originally the aim was to compare the effect of nitric acid, hydrochloric acid, perchloric acid and different heights of cationic exchange columns as acidic catalysts. From these sample the perchloric acid catalyzed experiment was discarded, due to the lack of gel formation. The samples were investigated by SEM.

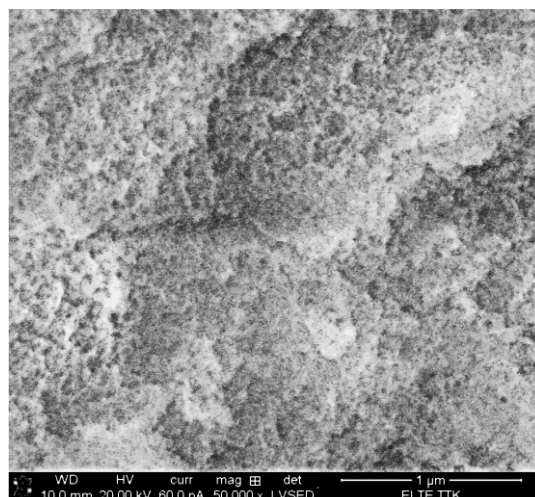
Hydrochloric acid



1 000x magnification



10 000x magnification



50 000x magnification

Figure 6. Scanning electron microscopy images taken from the cryogel prepared with hydrochloric acid

In the scanning electron microscopy micrographs the sample shows a relatively high inhomogeneity, both in the pore size distribution and the composition of the material. The pore size ranged from 4700 nm to 7200 nm for the macropores of the gels (1000x magnification), while the nanopores had a diameter between 65 and 72 nm (50000x magnification). The porosity

of the cryogel is comparable to the sample prepared with nitric acid as the catalyst, between 60-65 %. Though, as mentioned before, the cryogels actually showed a high level of inhomogeneity in their composition based on the 1000 and 10000 times magnifications, bright precipitations can be seen on the sample. This inhomogeneity was investigated using EDAX, which showed that the precipitations found on the 3D network of the gel, were NaCl salt precipitations. For this reason the usage of HCl as catalyst was discarded.

Cation exchange column – 10 cm

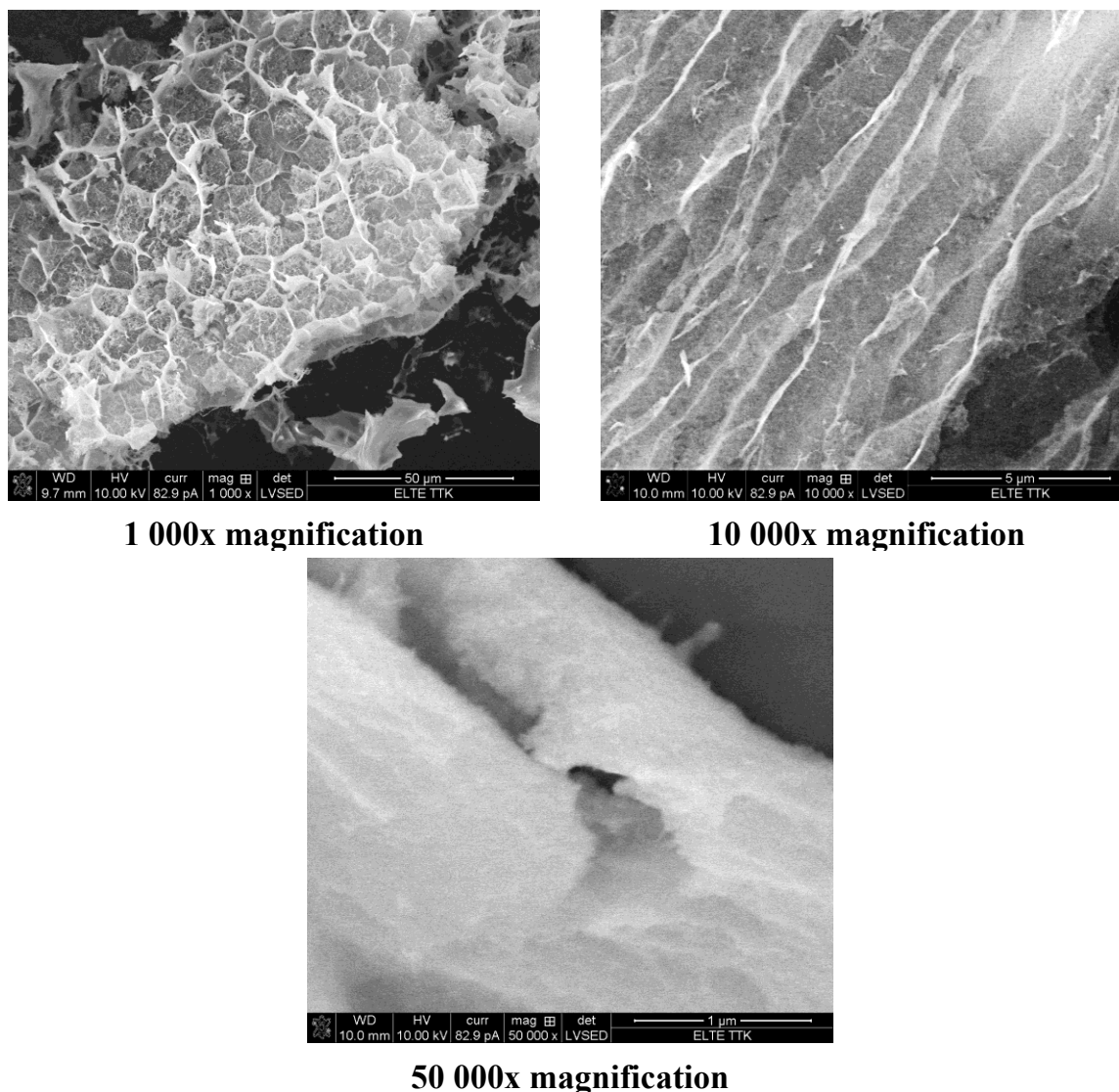
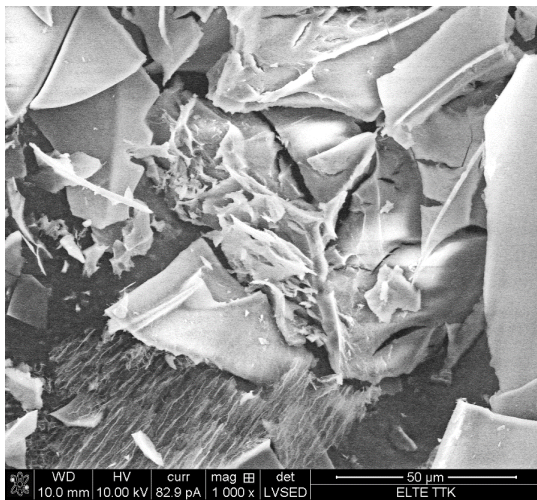


Figure 7. Silica cryogel prepared by ion exchange (1x10 cm column)

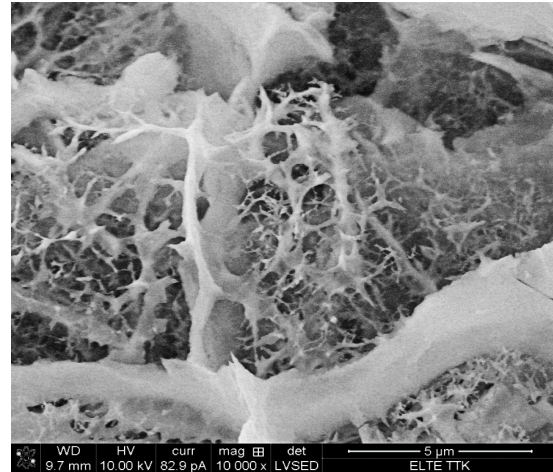
As already described in the fourth chapter, in this sample instead of using an acidic catalyst, a cation exchange column was used to set the pH of the system, initiating the gelation. The micrographs taken from the sample, show some level of inhomogeneity with a cellular morphology and loose three-dimensional structure. A hierarchical pore system can be observed

with macropores ranging from 9000 nm to 15000 nm (average of 11000 nm), and nanopores with a diameter of 400 – 800 nm inside the wall of macropores. The porosity of the cryogels ranges from 65 to 70 %, the average being 66%

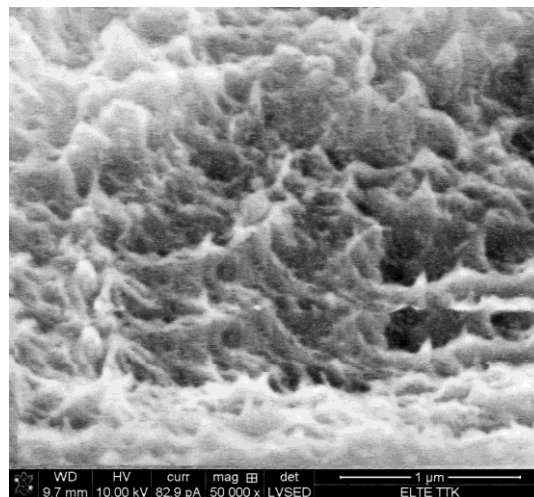
Cation exchange column – 1×10 cm + 1×15 cm



1 000x magnification



10 000x magnification



50 000x magnification

Figure 8. Silica cryogel prepared by ion exchange (1x10 + 1x15 cm column)

The scanning electron microscopy recordings showed the presence of a three-dimensional gel network, with a high level of inhomogeneity. The cellular morphology, present in the previous sample is not observable, but the mostly macro sized pores are ordered into columns. The average diameter of these pores, is between 2000 and 3000 nm, with a complete lack of nanopores, with a porosity of 65 – 70 %.

Summary of catalyst effect on cryogels derived from water glass by SEM investigation

Based on the scanning electron microscopy measurements, it is certain that the type of catalysis has a significant effect on the final morphology of the cryogels. It can influence the average pore size, their distribution, and their percentage compared to the gel network (porosity). Based on these experiments, the selection can also cause the appearance of unwanted side effects, like in the case of HCl catalyst, the formation of salt precipitations was observed on the 1000x and 10000x magnifications. The homogeneity of the sample can also greatly vary depending on the catalyst. This behavior was seen in both cryogels prepared by an ion exchange column, which resulted in some level of inhomogeneity.

Based on the results achieved in these measurements, seen in Table 5, nitric acid was selected as the catalyst of gelation going forward.

Table 9. Containing morphological properties of each sample prepared by different catalysis methods

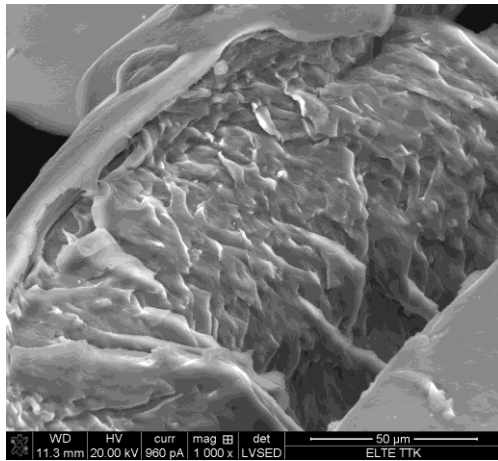
Precursor	Catalyst	pH	Porosity/ %	Pore size / nm	
				macropores	nanopores
10 w/w% sodium silicate solution	HNO ₃	9	55 - 60	-	20 - 200
	HCl	8	60 - 65	4766 - 7200	65 - 72
	10 cm high ion exchange column	6	65 - 70	9000 - 15000	400 - 800
	10 + 15 cm ion exchange co.	6	65 - 70	2000 - 3000	-

5.3 TEOS cryogels, the effect of solvent precursor ratio, and additives

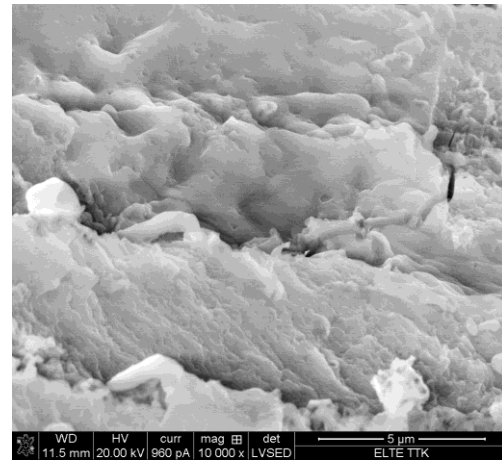
In the case of cryogels synthesized from TEOS solutions, the influence of precursor to solvent ratio, and the effect of different additives was investigated, by scanning electron microscopy. The recorded micrographs were used to determine average pore size, general morphology, and porosity of the gels.

Original recipe

The micrographs recorded from the sample show a high level of inhomogeneity, with pores ordered into channels. The porosity of the cryogel varies in the range of 40 – 60%, with macropores between 4000 – 5000 nm, and mesopores, with diameters around 40 – 400 nm.



1 000x magnification

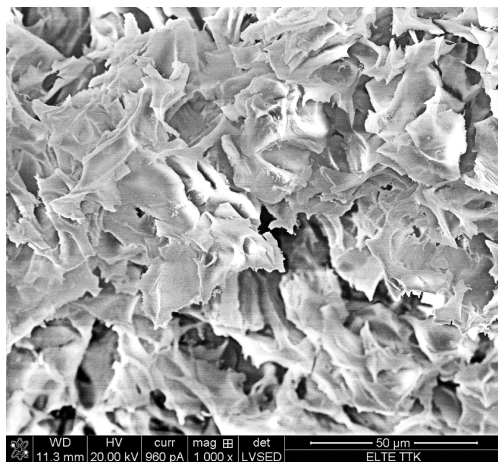


10 000x magnification

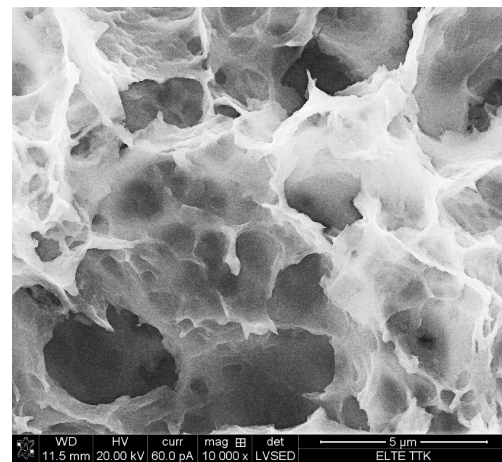
Figure 9. SEM images of silica cryogels (TEOS) synthesized by acidic catalyst

Modified solvent, precursor ratio

Based on the micrographs the sample proved to have similar morphological properties to the original recipe. Solvent mixture of ethanol and distilled water was investigated.



1 000x magnification

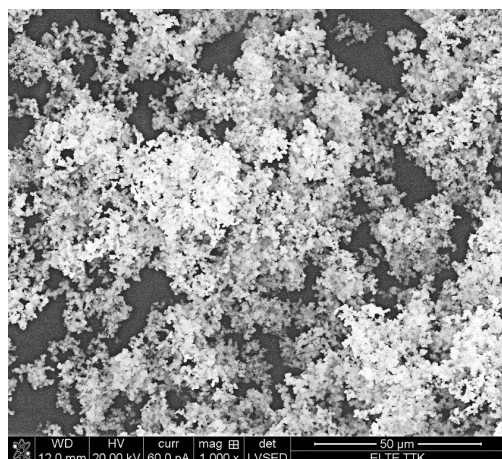


10 000x magnification

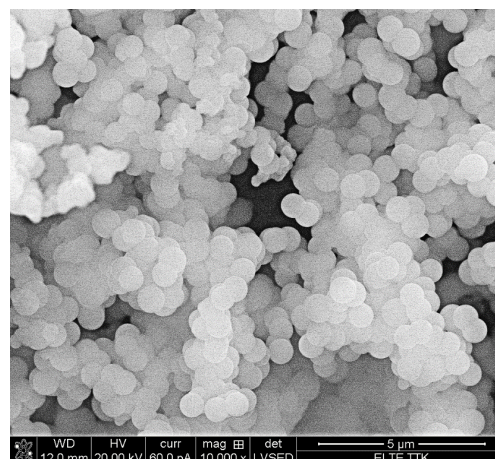
Figure 10. SEM images of silica cryogels (TEOS) synthesized by replacing half of the original alcoholic solvent with distilled water

A highly porous, three-dimensional structure is observable on the SEM images, typically with irregularly shaped macropores in the range of 5000 – 15000 nm. Although not characteristic, smaller macropores, in the range of 1000 – 3000 nm, and mesopores with an average diameter of 600 nm (distributed in the range of 300 - 1300), also appear in the gels. The average porosity of the gel ranges from 65 to 70%.

TEOS and NH₃ catalyst



1 000x magnification

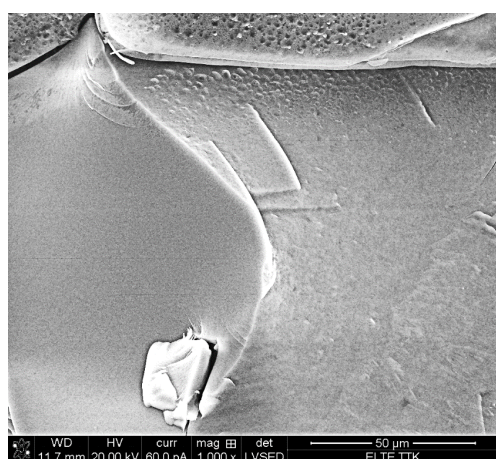


10 000x magnification

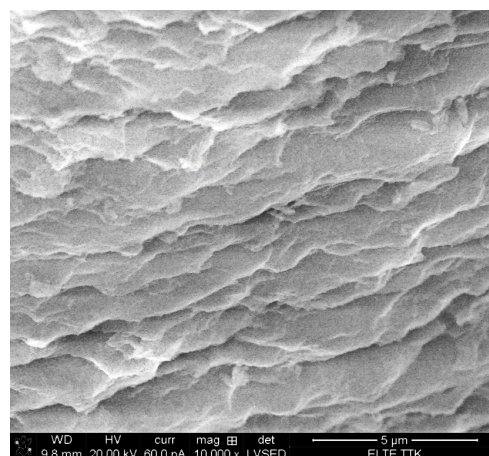
Figure 11. SEM images of silica cryogels (TEOS) synthesized by the addition of ammonia

The sample shows a distinct feature compared to other cryogels samples, due to its aggregate structure built up of regularly shaped spheres, with an average size varying between 600 and 800 nm. Between the particles, irregularly shaped macropores, with an average diameter of 10000 – 15000 nm, and mesopores, ranging from 500 to 3000 nm, are located. The average porosity of the sample is 38 – 58 %. It means that, this cryogel has one of the most compact structures.

TEOS + HNO₃ catalyst and citric acid additive



1 000x magnification



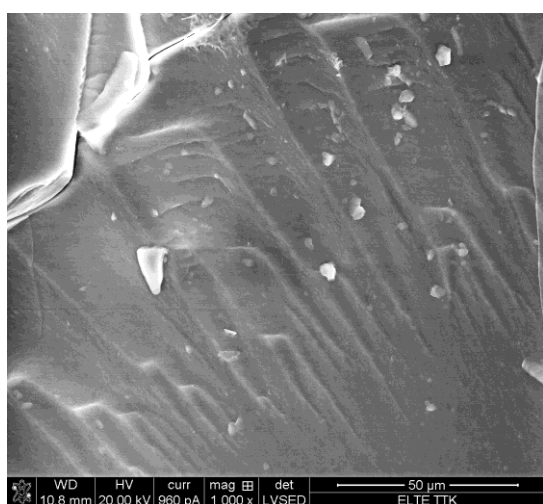
10 000x magnification

Figure 12. SEM images of a silica cryogel (TEOS) synthesized by the addition of nitric acid and citric acid

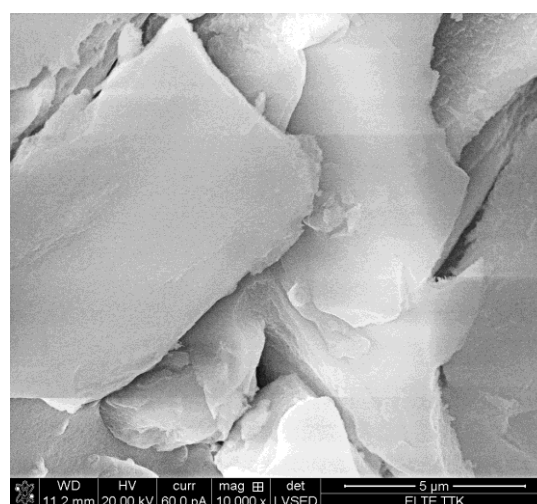
The cryogel shows a homogeneous, relatively compact, less porous structure than other TEOS based samples, with a porosity below 50%. Although macropores, with a size of 1 to 2 μm , are present in the system, these are not characteristic to the cryogel, since smaller mesopores are dominating. The size of these pores varies from 30 nm to 150 nm, with an average diameter of 90 nm. Due to its low porosity further usage of the gel was discarded.

TEOS + propylene-oxide gelation agent

Apart from having the highest gelation time of 120 hours, the cryogels show a rather compact structure with a negligible porosity of 10 to 20 %. The porosity is made up from mostly irregularly shaped macropores, ranging from 1.5 μm to 3.5 μm , and some nanopores scattered around with a diameter of 30 to 60 nm. Due to the high gelation time and poor porosity the sample was discarded.



1 000x magnification



10 000x magnification

Figure 13. SEM images of a silica cryogel (TEOS) synthesized by the addition of propylene oxide

Summary of cryogels derived from TEOS by SEM investigation

The experiment proves that the gelation time can be greatly reduced by altering the solvent to precursor ratio. By decreasing the amount of ethanol added to the tetraethyl orthosilicate solution, the gelation time was lowered from 72 hours to 2 hours, without any significant change in the final cryogel sample. It was also proved that by replacing half of the alcoholic solvent with distilled water, the porosity can be greatly improved, increasing from the original 40-60 % range to 70 %. Although the sample still has drawbacks compared to water glass based solutions, like the domination of bigger macro pores. The SEM recordings show it certainly, that the structure of the gels can be greatly influenced by the addition of different materials

during the sol-gel process, with most additives making the gels more block like and compact. All measured qualities are summarized in the table below.

Table 10. Physical properties of TEOS based cryogel series, determined by the SEM images

Precursor	Molar ratio of TEOS : solvent	catalyst	additive	Porosity / %	Pore size / nm	
					macropores	nanopores
alcoholic solution of TEOS	1 : 10	HNO ₃	-	40 - 60	4000 - 5000	40 - 400
	1 : 4	HNO ₃	-	40 - 60	4000 - 5000	40 - 400
	1 : 4	HNO ₃	citric acid	<50	1000 - 2000	30 - 150
	1 : 4	-	NH ₃	38 - 50	10000 - 15000	500 - 3000
	1 : 4	-	propylene oxide	10 - 20	1500 - 3500	30 - 60
water – alcohol	1 : 4	HNO ₃	-	70	5000 - 15000	300 - 1300

5.4 Composite systems – SEM images

In the case of composite systems, the main goal was to determine the effect of the concentration of either NaOH, carbamide, or both, and whether the addition of HEC had any influence on the reaction between the cellulose and cryogels. The samples were investigated with scanning electron microscopy, to observe the homogeneity of the composite and the surface of the fibers, while infrared spectrometry was used to determine the bond structure of the systems.

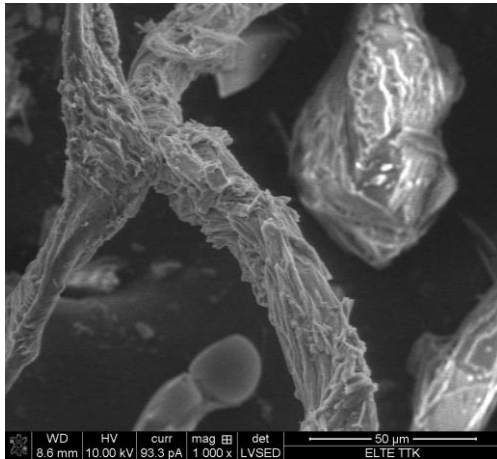
5.4.1 Difference between cotton and pure cellulose fibers as the matrix

To find the difference between composite systems formed with cotton and pure cellulose fibers, two distinct materials were formed. Both systems used a solvent mixture containing 2 mol/dm³ NaOH and 2 mol/dm³ carbamide for partially dissolving the corresponding fibers. In the first, cotton was used as the matrix, while in the second system pure cellulose fibers were utilized.

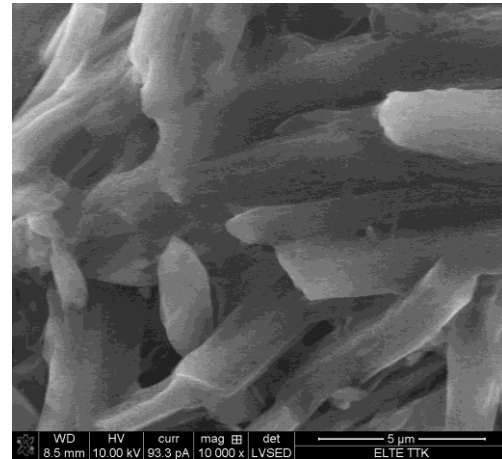
Silica cryogel (water glass, pH 9) + cotton fibers, 2M NaOH - 2M carbamide solvent

The SEM images of the sample are showing the preservation of the original cellulose fibers in the composite, small platelets with an average diameter of 1 – 2 μm appeared on the surface of the fibers. The composition of these platelets was investigated by the EDAX detector of the

instrument, which showed a high amount of Na and C in the region, meaning that these crystal precipitations originate from the cellulose fibers.



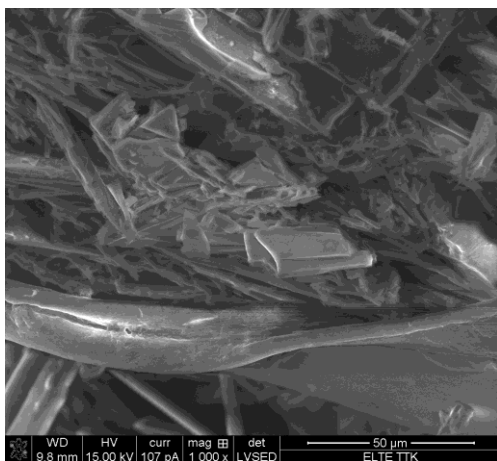
1 000x magnification



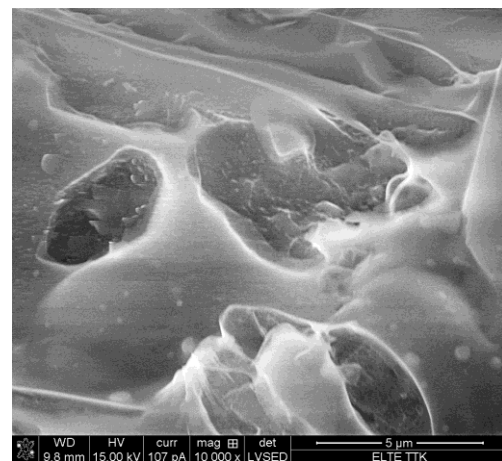
10 000x magnification

Figure 14: Scanning electron microscopy recordings of a composite containing silica cryogels (water glass, pH 9), cotton fibers, NaOH, carbamide (2M NaOH, 2M carbamide)

Silica cryogel(water glass, pH 9) + *pure cellulose* fibers, 2M NaOH-2M carbamide solvent



1 000x magnification



10 000x magnification

Figure 15. Scanning electron microscopy recordings of a composite containing silica cryogels (water glass, pH 9), viscose fibers, NaOH, carbamide (2M NaOH, 2M carbamide)

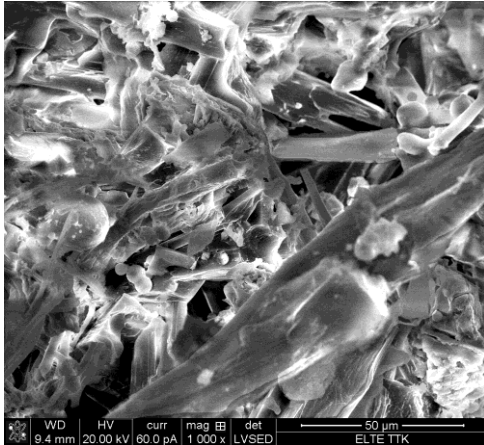
Compared to the previous sample the presence of whole fibers is rare, with porous structures and rod like formations dominating the sample (seen on the 1000x magnification). Intact fibers can still be found in the micrographs, with an average diameter of 5 μm. It can be seen on most recorded images that highly porous structures are dominating the sample, with an average size of 50 – 130 μm(based on the 500x magnification), and pore size scattered between 200 and 780 nm (determined by higher magnifications of 10 000x).

Summary of composite systems prepared with cotton and pure cellulose

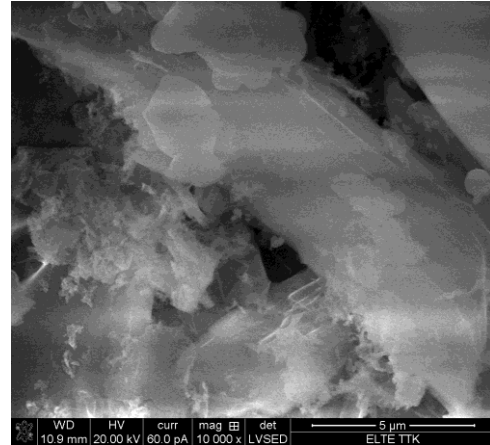
The SEM images verified the previously seen inhomogeneity of the composite prepared by cotton fibers, with whole fibers scattered all around the sample. At the same time the scanning results showed a high level of homogeneity, with most of the structure being highly porous structures in the sample prepared with pure cellulose.

5.4.2 pure cellulose fiber + cryogel (TEOS) + solvent mixture, and HEC

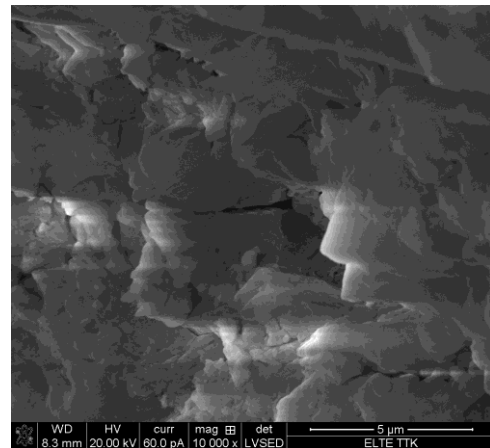
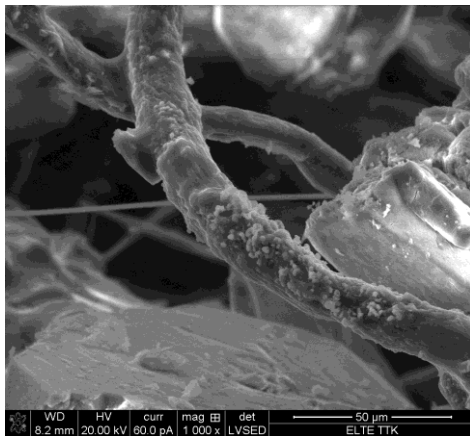
1 000x magnifications



10 000x magnifications



Silica cryogel (TEOS) + viscose fibers, 5M NaOH - 2M carbamide



Silica cryogel (TEOS) + viscose fibers, 5M NaOH - 2M carbamide + HEC

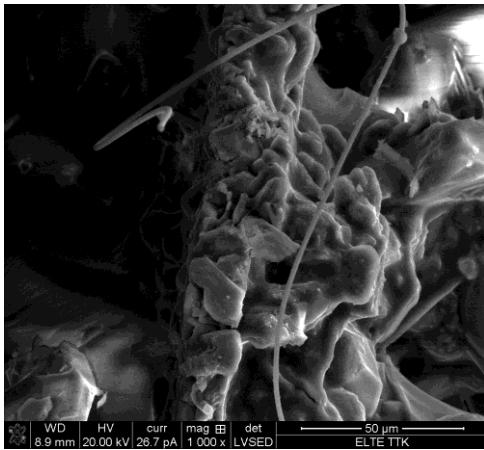
Figure 16. SEM images of composite systems prepared from silica cryogel (TEOS), NaOH-carbamide solution (5M NaOH, 2M carbamide), and HEC. The left side contains images with 1000x magnification, the right side contains images with 10000x magnifications

From the scanning electron microscopy images (Figure 15.) it can be determined that from the two composite systems prepared from TEOS cryogels, the sample without HEC shows no clear signs of reaction taking place on the surface of the fibers, apart from the precipitation of some

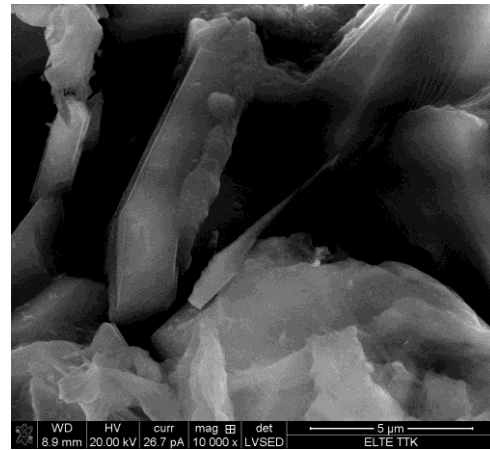
cryogel particles, while the sample with HEC has signs of reaction on the surface, as seen on the 1000 times magnifications of both composites. This magnification makes it viable to determine the diameter of the cellulose fibers. In both cases the fibers have an average diameter of 4-5 μm .

5.4.3 Pure cellulose fiber + cryogel (water glass, pH 9) + solvent mixture, and HEC

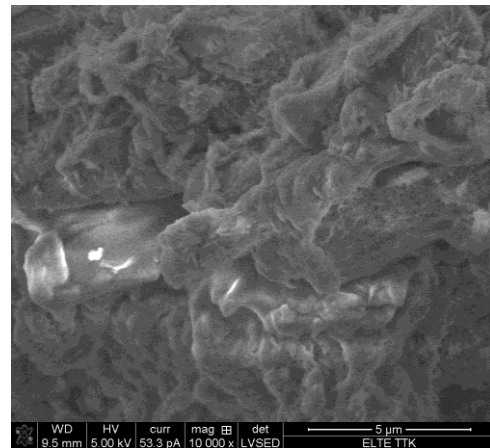
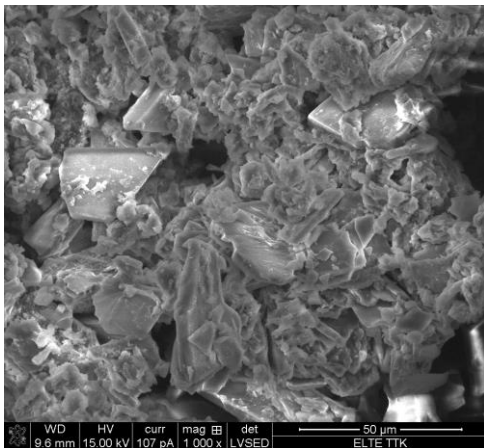
1 000x magnifications



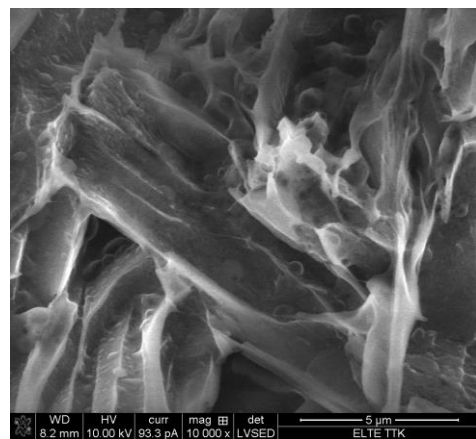
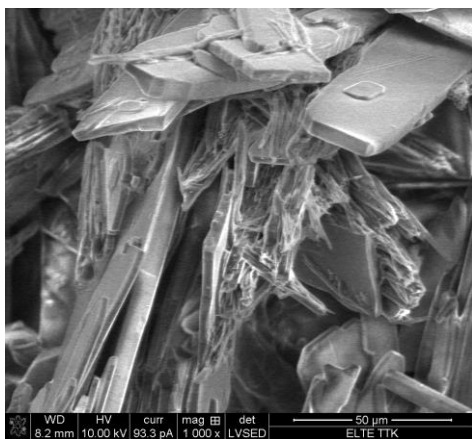
10 000x magnifications



Silica cryogel (TEOS) + viscose fibers, 5M NaOH - 2M carbamide + HEC



Silica cryogel (water- glass, pH 9) + viscose fibers, 5M NaOH - 5M carbamide

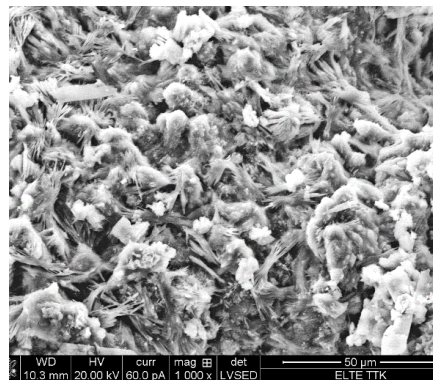


Silica cryogel (water- glass, pH 9) + viscose fibers, 5M NaOH - 5M carbamide + HEC

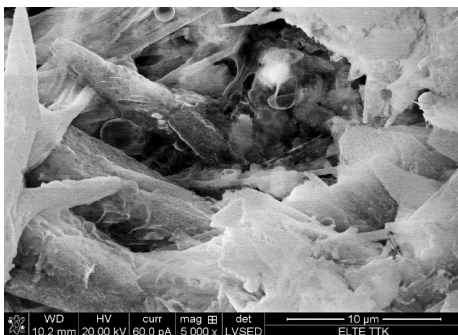
Figure 17. composite systems prepared from silica cryogels (water glass, pH 9), NaOH-carbamide solvent, and HEC

Figure 17. shows the scanning electron microscopy images taken from the composite materials, prepared from water glass based silica cryogels (pH 9). The first sample, with 5M NaOH and 2M carbamide, and HEC as an additive, shows a highly inhomogeneous structure with both intact, and reacting fibers, both seen on the 1000x magnification. The average fiber width is around 1-2 μm , with some even smaller fibers (1000x magnification). Increasing the concentration of carbamide to 5 mol/dm³, with HEC still used as an additive, resulted in a more homogeneous structure built up from plates and porous, amorphous particles, with an average size of 10-20 μm (1000x magnification). Increasing the magnification to 10000x, reveals even smaller porous particles with an average size of 1-2 μm . Removing the HEC from the composition, but keeping the solvent composition, resulted in a lack of visible fibers, with highly porous aggregates dominating the structure. There is a wide range of three-dimensional particles appearing, with small nano-sized particles between 30-70 nm and micro-sized particles with a size of 20-30 μm .

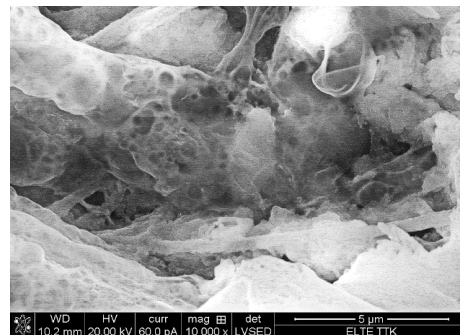
5.4.4 cellulose fiber + cryogel (water glass, pH 1) + solvent mixture, and HEC Silica cryogel(water glass, pH 1) + *pure cellulose* fibers, 5M NaOH - 5M carbamide



1 000x magnification



5 000x magnification



10 000x magnification

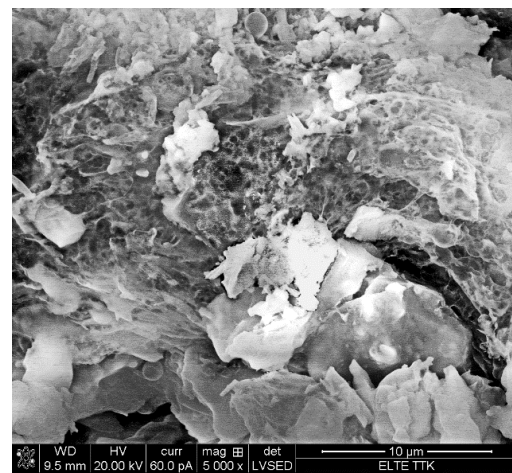
Figure 18: Scanning electron microscopy recordings of a composite containing silica cryogels (water glass, pH 1), viscose fibers, NaOH, carbamide (5M NaOH, 5M carbamide)

The SEM images of the sample can be seen on figure 18. The composite synthesized this way shows a more compact nature than the raw cryogels (with pH =1), but still relatively high porosity. The 1000x magnification of the sample presents a homogeneous structure of broken cellulose fibers, with a relatively narrow size distributions in the range of 2 to 3 μm , and smaller cryogel particles stuck to their surface. Increasing the magnification to 5000 – 10000 times, reveals a clear proof of reaction taking place on the fibers, and a level of inhomogeneity inside the sample with the appearance of thinner cellulose fiber remains. These fiber remains have an average width of 0.5 μm .

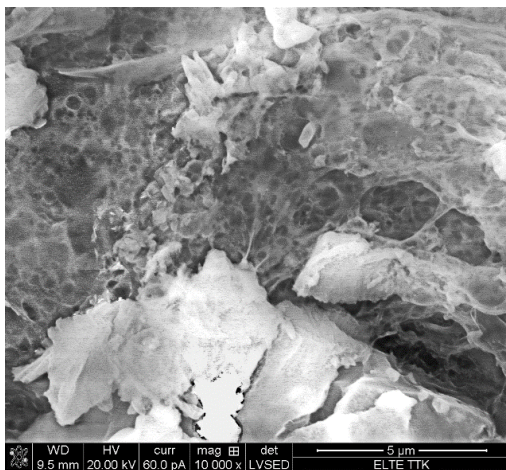
Silica cryogel(water glass, pH 1) + pure cellulose fibers, 5M NaOH - 5M carbamide + HEC



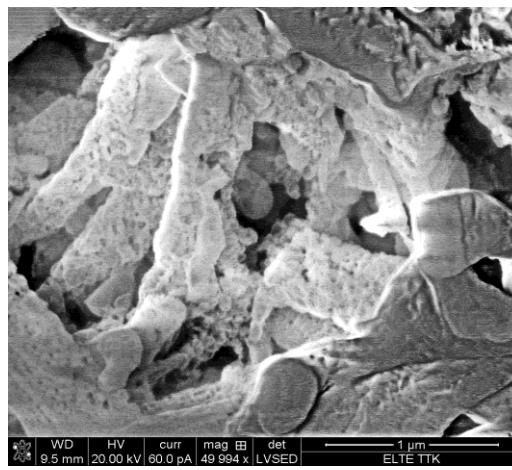
1 000x magnification



5 000x magnification



10 000x magnification



50 000x magnification

Figure 19: Scanning electron microscopy recordings of a composite containing silica cryogels (water glass, pH 1), viscose fibers, NaOH, carbamide (5M NaOH, 5M carbamide) and HEC

The sample shows a relatively higher level of inhomogeneity, with bigger porosity than the previous composite, without HEC. The 1000 times magnification presents an inhomogeneous structure with the presence of both intact cellulose fibers (the big fiber in the middle, 1000x), and smaller pieces of fibers scattered around, broken during the synthesis. The intact fibers have a width of 18 μm , while a higher magnification (50 000x) reveals a 0.5 micrometer average width for the broken fibers. This magnification also shows that the reaction on the fiber surface is much stronger than in the case of the composite without HEC.

Silica cryogel(water glass, pH 1) + cellulose textile

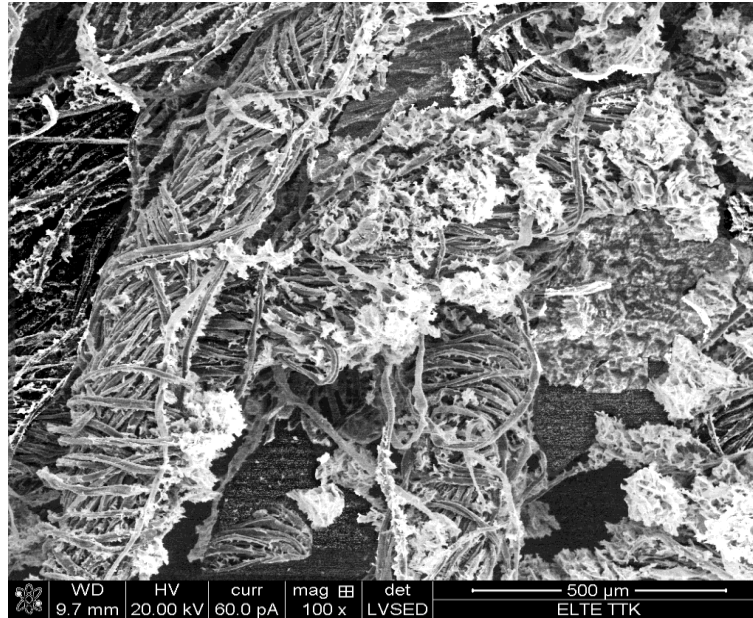
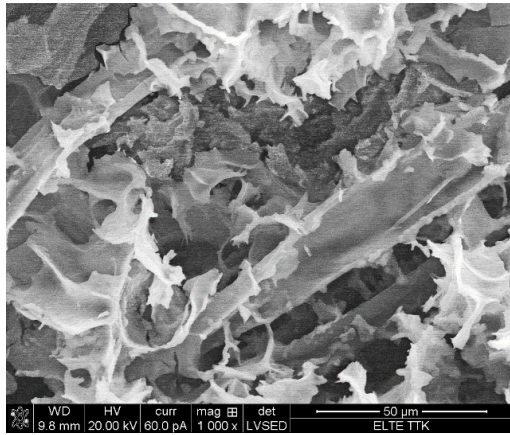
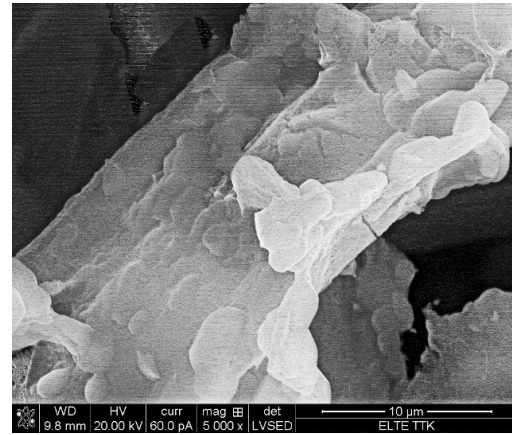


Figure 20: 100 times magnification of a composite formed between textile and silica cryogels (water glass, pH 1)

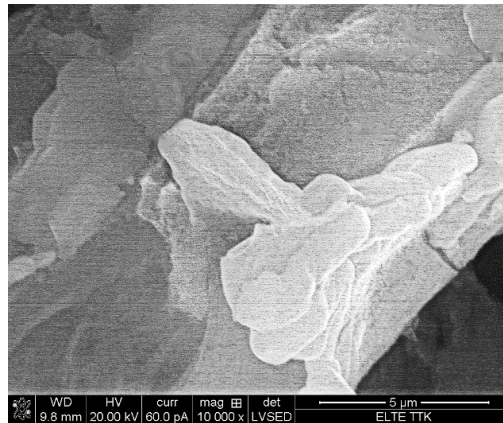
Since the cellulose fiber was added to the system right before the freeze drying process, the sample shows a much looser cryogel structure than the other two composite materials. On the lower magnification image(100x) the general structure of the reinforcing textile can be seen as a woven material made from smaller fibers. In this case, due to the NaOH – carbamide treatment, the decomposition of these fiber bundles is observable. With an increasing magnification, cryogel particles sticking to the fibers are seen. This phenomenon is observable on magnifications: 1000x, 5000x and 10000x.



1 000x magnification



5 000x magnification



10 000x magnification

Figure 21: Scanning electron microscopy recordings of a composite containing silica cryogels (water glass pH 1), textile

5.5 Composite materials – FT-IR

5.5.1 Silica cryogel (water glass, pH 1), cellulose fibers and HEC

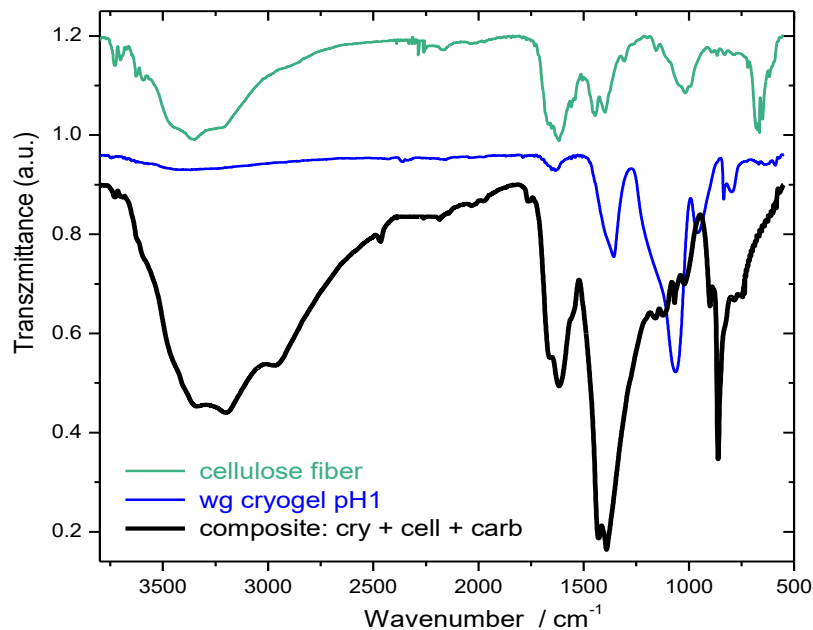


Figure 22. FT-IR spectra of the composite prepared from silica cryogel (water glass, pH 1), viscose fibers and NaOH, carbamide (5M -5M), with the cellulose fibers spectra (green) and cryogel's spectra (blue).

IR evaluation of composite derived from silica cryogel (water glass, pH 1), cellulose fibers (5M NaOH, 5M carbamide):

- At 2960 cm^{-1} a new peak appear, which is not present in the spectra of the cryogel or the cellulose fiber. This peak can be attributed to the valence vibration of a bonded hydroxyl group in hydrogen bond with a carbon atom (ν_{C-OH}).
- A new peak also appears at 862 cm^{-1} , which is not present in the cryogel's spectra or the spectra of cellulose. This peak is the asymmetric vibration of the Q^0 dissolved silica species. This is a molecule where the polymeric chains of the silica are replaced by OH groups forming $\text{Si}(\text{OH})_4$.
- The two peaks in the composite's spectra, at 1618 cm^{-1} and 1658 cm^{-1} , come from the viscose fiber. The first peak is the OH bending, while the second peak at 1658 is the stretching vibration of C=O bonds from the cellulose. These peaks are not shifted in the spectra of the composite, compared to the cellulose fiber's spectra
- At 1387 cm^{-1} the peak corresponds to the peak of $\text{Si}(\text{OH})_4$ in hydrogen bonds from the cryogel's spectra. This peak is shifted compared to the original wavenumber of the cryogel (1364 cm^{-1})

- An other shifted peak can be observed at 1427 cm^{-1} , originated from the HCH, OCH bending of the cellulose spectra, located at 1449
- The shifted peaks further prove the existence of connection formed between the matrix and reinforcement phase.

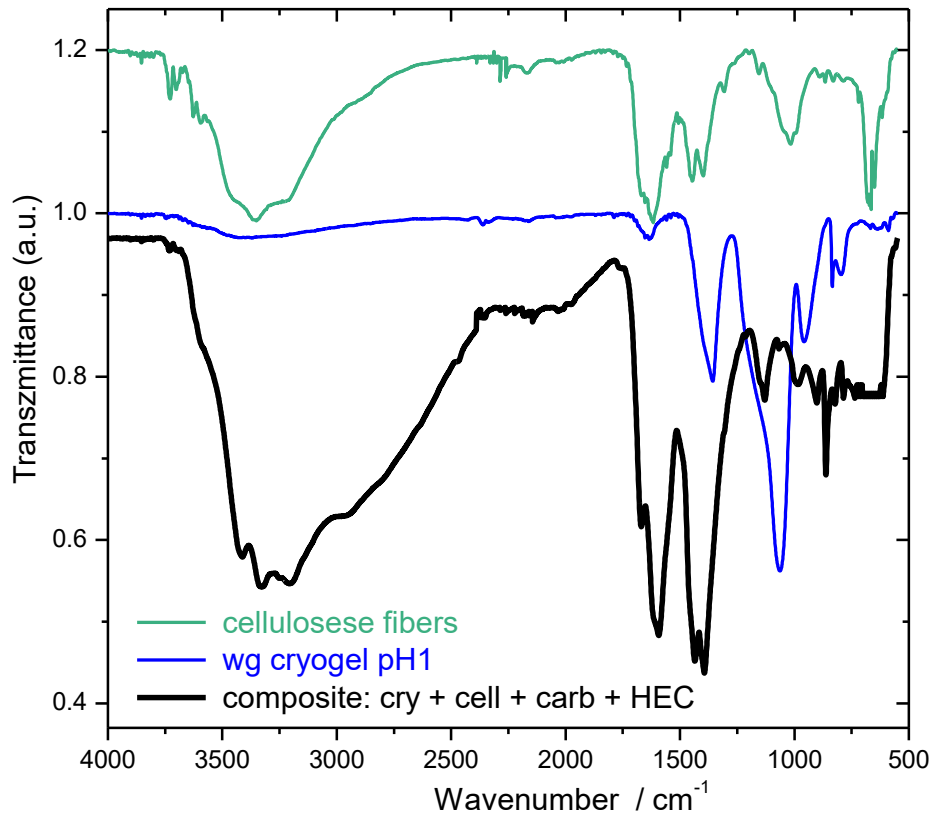


Figure 23: FT-IR spectra of the composite prepared from silica cryogel (water glass, pH 1), viscose fibers and NaOH, carbamide (5M -5M) and HEC, with the cellulose fibers spectra (green) and cryogel's spectra (blue)

IR evaluation of composite derived from silica cryogel (water glass, pH 1), cellulose fibers and HEC (5M NaOH, 5M carbamide)

(Figure 23.)

- The new peaks appearing in the composite without HEC, are also observable in this sample, at 2957 cm^{-1} and 864 cm^{-1} respectively, with the shifted peaks also present. In this case the peak originated from the cryogel, $\text{Si}(\text{OH})_4$ in a hydrogen bond appears at 1386 , shifted from its original position at 1367 . The peak, coming from the cellulose appears at 1435 , from its original position at 1448 (bending of HCH, OCH)
- A new peak is observable at 1132 cm^{-1} , which was not present in the previous sample. This peak can be further divided into two other peaks. The first one is asymmetric vibration of Si-

O-C bonds at 1135, while the second peak is at 1152, the asymmetric vibration of C-O-C bonds.

- The peaks originated from the OH bending, and stretching vibration of C=O bonds of the viscose fiber remained at their original wavenumbers similarly to the previous sample.
- The peak found at 1060 cm^{-1} on the original spectra of the cryogel drastically decreased in intensity. This peak is associated with the Si-O-Si bonds.
- Based on these IR spectra, it is proven that in both cases, certain reaction happens between the two phases, with new peaks appearing and existing peaks shifting. The measurement shows a much stronger when the sample included HEC as an additive, due to the appearance of more new bonds, with the decrease of Si-O-Si bonds further proving this fact

5.5.2 silica cryogel (water glass, pH 9), cellulose fibers, and HEC

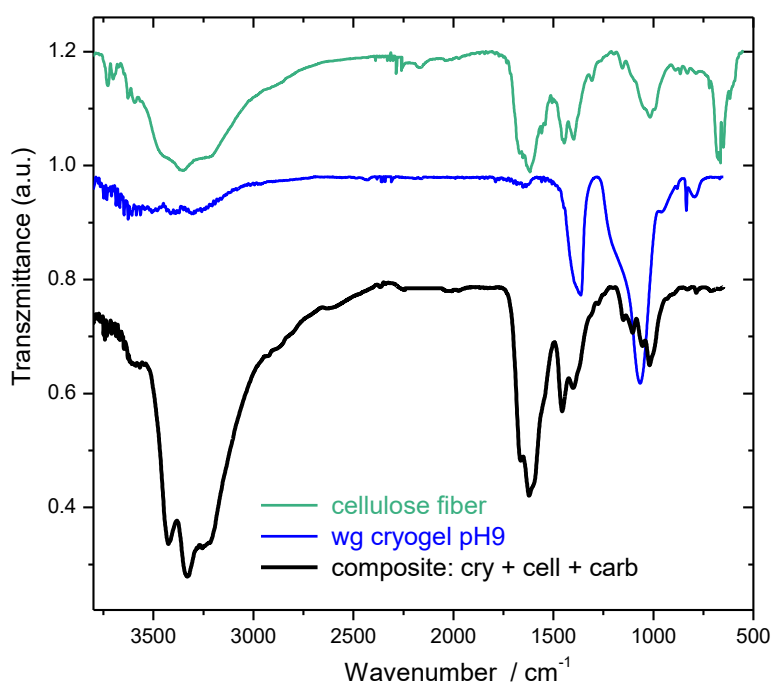


Figure 24: FT-IR spectra of the composite prepared from silica cryogel (water glass, pH 9), viscose fibers and NaOH, carbamide (5M -5M), with the cellulose fibers spectra(green) and cryogel's spectra (blue)

IR evaluation of composite derived from silica cryogel (water glass, pH 9), cellulose fibers (5M NaOH, 5M carbamide):

(Figure 24.)

- Compared to the previous sample with pH 1 cryogel, the most notable difference is the lack of peaks at 2960 cm^{-1} , 862 cm^{-1} and 1132 cm^{-1} .

- The peak at 1661 cm^{-1} is originated from the cellulose fiber. This is associated with the stretching vibration of C=O bonds. There is a peak, also coming from the cellulose, at 1617, corresponding to the OH bending. These two peaks are showing no real shift compared to the original position.
- Similarly to the pH 1 sample, two peaks, with shifted wavenumbers can be seen at 1461 cm^{-1} and 1397 cm^{-1} , but in this sample they are much more muted compared to the characteristic peaks at the pH sample. The 1461 cm^{-1} peak is associated with HCH, OCH bending, while the peak at 1397 is Si(OH)₄ in hydrogen bond.
- The peak found at 1067 (Si-O-Si bonds), also decreased much less compared to the previous sample
- Based on this evaluation the sample with cryogel prepared in pH 1 environment formed much more bonds with the matrix of the composite system. Resulting in a stronger interaction between the reinforcement and matrix.

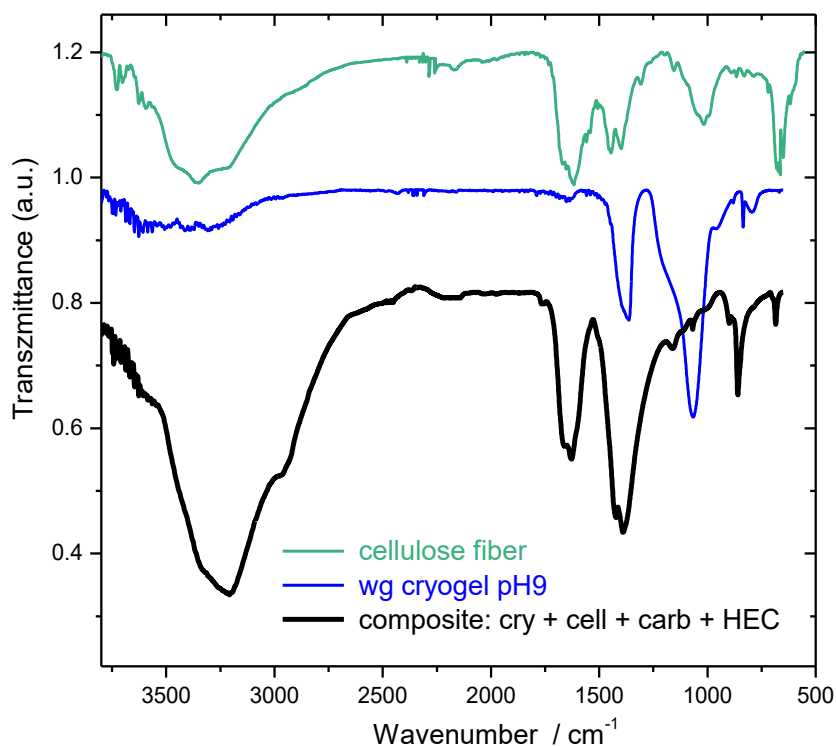


Figure 25: FT-IR spectra of the composite prepared from silica cryogel (water glass, pH 9), viscose fibers and NaOH, carbamide (5M -5M) and HEC, with the cellulose fibers spectra (green) and cryogel's spectra (blue)

IR evaluation of composite derived from silica cryogel (water glass, pH 9), cellulose fibers and HEC (5M NaOH, 5M carbamide) (Figure 25.):

- The IR spectra shows the appearance of a peak at 2966 cm^{-1} as a small shoulder. This was missing from the sample without the addition of HEC, but was found in both composites

prepared with pH 1 water glass cryogels. This is the valence vibration of the OH group, in hydrogen bond.

- The peaks at 1662 and 1629 cm^{-1} , were present in all previous composite systems without shifting, like here. Both of these peaks are coming from the cellulose. Compared to the sample without HEC (pH 9) the peaks are more characteristic, but still muted compared to the pH 1 samples.
- The peak corresponding to the HCH, OCH bending, of the viscose fiber, is also observable with a shift at 1415 cm^{-1} , compared to the original position of 1442 (in the case of pH 1 it was at 1427). With the cryogel's Si(OH)₄ peak also appearing with a shift, at 1384 cm^{-1}
- With the addition of HEC, the previously, also missing peak, corresponding to Q⁰ also appeared at 848 cm^{-1} .
- Although the addition of HEC improved the number of bonds between the cryogel and matrix, it is still far from the number of bonds forming in the case of the pH=1 sample.5.5.3 silica cryogel (TEOS), cellulose fibers, and HEC

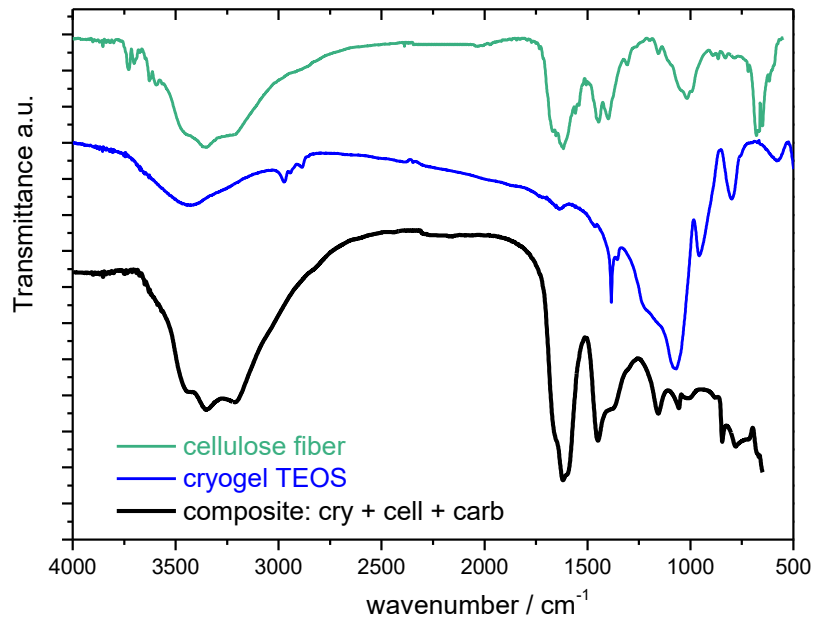


Figure 26: FT-IR spectra of the composite prepared from silica cryogel (TEOS), viscose fibers and NaOH, carbamide (5M -2M), with the cellulose fibers spectra (green) and cryogel's spectra (blue)

IR evaluation of composite derived from silica cryogel (TEOS), cellulose fibers, carbamide, (5M NaOH, 2M carbamide) (Figure 26.):

- The peak that appeared in the water glass based composite (pH=1), is missing in this spectra, with peaks above 3000 cm^{-1} , belonging to the cellulose fibers.

- At 1657 a slightly shifted peak appears, corresponding to the stretching vibration of C=O bonds from the viscose fiber (originally at 1663 cm^{-1}). As the shoulder of the peak, the OH bending of the viscose fiber is also present at 1657 cm^{-1} (originally at 1663 cm^{-1}). Both appears with much less shift compared to composite systems prepared from water glass based cryogels.
- The HCH, OCH bending peak of the cellulose is observable without shift at 1451 cm^{-1} .
- A new peak is seen at 1157 cm^{-1} , not present in the fiber, and only observable as a shoulder of an other peak on the spectra of the cryogel. This is associated with...
- Significant peak of the cryogel corresponding to the Si-O-Si bonds, is much less prevalent on the composite's spectra, as seen at 1057 cm^{-1} . This partially proves the presence of reaction, due to the decrease in the number of Si-O-Si bonds.
- This is further verified by the deformation of the peaks at 845, and 775 cm^{-1} . These peaks are originated from the TEOS cryogel's Si-O bonds, and asymmetric vibration of the Si-O-Si bonds respectively.

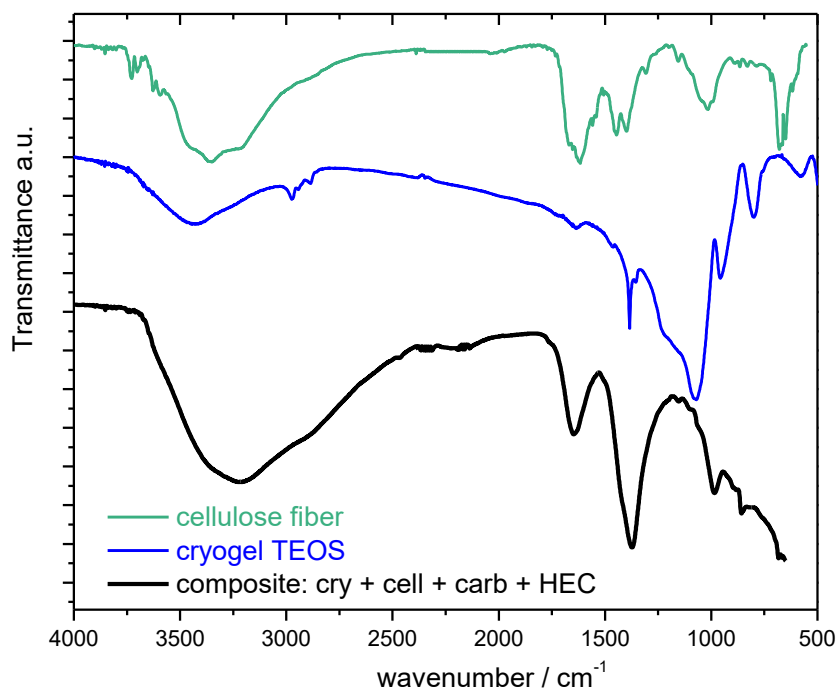


Figure 27: FT-IR spectra of the composite prepared from silica cryogel (TEOS), viscose fibers and NaOH, carbamide (5M -2M) , with the cellulose fibers spectra, and HEC(green) and cryogel's spectra (blue)

IR evaluation of composite derived from silica cryogel (TEOS), cellulose fibers, carbamide, and HEC (5M NaOH, 2M carbamide) (Figure 27.):

- Compared to the sample prepared with the same composition but without the addition of HEC, a slight peak shoulder appears at 2930 cm^{-1} stretching to 2400 cm^{-1} . This is the same peak that was present in the case of water glass based silica cryogels (both pH 1 and pH 9), corresponding to the valence vibration of a hydroxyl group in a hydrogen bond.
- At 1640 cm^{-1} and 1663 cm^{-1} two peaks are observable originating from the cellulose. The peaks are the OH bending and stretching vibrations of the C=O bonds respectively.
- With the addition of HEC a new, quite strong peak is present at 1370 cm^{-1} (in the sample without HEC only a peak shoulder was present). This peak is from the Si(OH)_4 , which is further verified by the decrease in intensity of the 1074 cm^{-1} peak of the original spectra of the cryogel.
- The peak, at 989 cm^{-1} can be attributed to the vibration of Si-OH bonds from the cryogel (originally present at 947 cm^{-1}), or the 1017 cm^{-1} peak originated from the cellulose.
- As observed in all previous examples, the addition of HEC significantly improved the reaction between the cellulose and cryogel, with the disappearance of the 1070 peak further proving this effect.

5.5.4 Conclusion of bond structure developed in the composite materials investigated by FT-IR

In all, investigated composite samples, the IR spectra showed a much more intense reaction, with the addition of HEC and NaOH, carbamide solution to the system. The reduction of the Si-O-Si bond's peak (1070 cm^{-1}), proves the presence of reaction, with the appearance of peaks at around 2960 , 1370 , and 980 cm^{-1} further verifying this fact. The sole addition of HEC, without NaOH, carbamide did not result in such, strong reactions, as seen on the figure below, where the spectra of a composite sample without HEC, with HEC and without NaOH, carbamide was recorded. The figure shows the lack of multiple peaks, that were present in the case of other composite systems, including the valence vibration of OH groups in hydrogen bonds at 2960 cm^{-1} . From the three composite, cryogels tried in composite materials, the water glass based cryogel (pH 1) proved to be the best reinforcing phase in the composite, due to the presence of multiple peaks that are not present in any other composition.

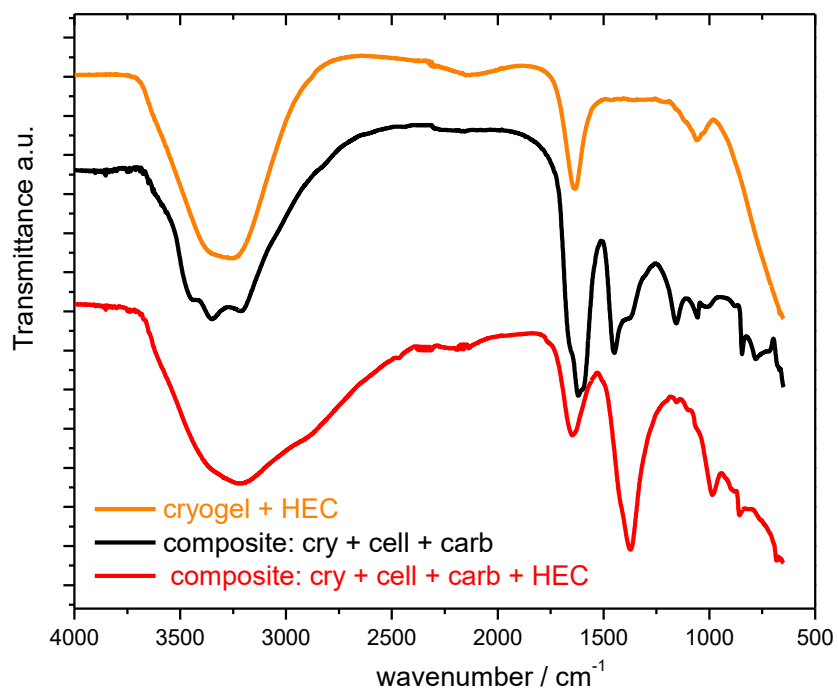


Figure 28: Spectra of three distinct composite compositions: cryogel + HEC (yellow), cryogel + cellulose + NaOH, carbamide (black), cryogel + cellulose + NaOH, carbamide + HEC (red)

5.6 composite materials – conduction measurements

Samples prepared with water glass based silica cryogels (pH = 1) were tested for their conduction capacity to verify their insulator nature. For the measurement, a 10 x 10 cm block of composite was prepared with a width of 1.5 cm from the sample with textile as reinforcement, and the NaOH, carbamide solution (5M -5M for both) based systems with and without HEC as an additive. The heat conduction capacity was measured at 20, 50 and 100 °C, the results are summarized in the Table 11. For comparison the data of Rockwool’s mineral wool was also added to the table.

The composite system prepared from pure cellulose textile, water glass - pH 1 - based silica cryogels particles, and solution of 2M NaOH-2M carbamide, provides the best heat conductivity value. The 0.042 W/m’K value is very similar to the value of commercial mineral wool (Rockwool’s product).

The heat conductivity was measured at Budapest Főváros kormányhivatala/ Metrológiai és Műszaki Felügyeleti Főosztály/ ElektromosHőfizikai és Optikaia Mérések Osztály.

Table 11. Summary of heat conductivity measurements

cryogel	NaOH-carbamide / mol/dm ³		HEC	Heat conductivity					
	NaOH	carb.		temp	λ / W/m’K	temp	λ / W/m’K	temp	λ / W/m’K
water glass (pH 1)	2	2	-	20 °C	0.042	50 °C	0.044	100 °C	0.047
	5	5	-		0.078		0.078		0.079
	5	5	+		0.072		0.074		0.078
Rockwool wool					0.039		0.040		0.041

6. SUMMARY

Biodegradable composites derived from silica cryogels and cellulose

Horváth Marius, MSc student in Material Science

Supervisor: **Dr. Sinkó Katalin** associate professor

In my research work, the aim was to develop of new, low-cost synthesis route for biodegradable thermal insulation layers for coating of geometry-free surfaces. The basic materials of the layer the silica cryogel. Cryogels must be applied in composite systems in order to obtain a monolithic structure. Our experiment, the cellulose fibers or textile provided the matrix of composites, and the silica cryogels the reinforcement phase.

During my research I synthesized silica cryogels from two type of precursors (water glass and TEOS), with distinct reaction parameters, like the type of acidic catalyst, reaction pH, precursor to solvent ratio and additives. In the case of water glass precursors, the effect of different type of acidic catalysts (HNO₃, HCl, and perchloric acid) and ion exchange were investigated. The structure and the morphology were characterized by scanning electron microscopy. Based on the SEM images, the sample prepared by perchloric acid formed precipitations instead of gels, while the HCl sample showed the formation of salt precipitations on the gel network. The application of ion exchange leads to production of inhomogeneous samples. The HNO₃ proved to be the most suitable catalyst.

In the next task, the effect of pH was investigated (pH 1, 3, 9, 11). With an increasing pH it was found that the average porosity of the cryogels decreased significantly, while the distribution of pore size got wider. The scanning electron microscopy images show the most homogeneous and porous structure for the sample with pH=1, so this was selected from the water glass based cryogels.

In the case of TEOS based cryogels, first the solvent to precursor ratio was adjusted from 10:1 to 4:1, which reduced the gelation time significantly. Citric-acid and ammonia were also tested as additives to the gel, but samples prepared by these additives were quite compact.

To achieve a better connection between the matrix and reinforcement phases, different additives were used, including a solvent mixture of NaOH and carbamide, and hydroxyethyl cellulose (HEC). The use of more crystalline and less crystalline cellulose forms have also been investigated, the less crystalline cellulose fiber or textile resulted in more homogeneous structure and better connection between cellulose and silica.

Over the SEM measurements, infrared spectroscopy is also served for determination of bond systems in the samples. The presence of HEC and the increasing concentration of both NaOH and carbamide improve considerably the reaction between the matrix and reinforcement. The IR measurement showed that, cryogels prepared in reaction medium with a pH = 1 (water glass based) form the highest number of bonds with the matrix.

The best heat conductivity value could be measured in the composite system prepared from pure cellulose textile, water glass - pH 1 - based silica cryogels particles, and solution of 2M NaOH-2M carbamide. The 0.042 W/m²K value of composite is very similar to that of commercial mineral wool (Rockwool's product).

NYILATKOZAT

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ELTE Természettudományi Kar, szak: Anyagtudomány MSc

NEPTUN azonosító: HR7C6V

Diplomamunka címe:

Biodegradable composites derived from silica cryogel and cellulose

A **diplomamunka** szerzőjeként fegyelmi felelősségem tudatában kijelentem, hogy a dolgozatom önálló szellemi alkotásom, abban a hivatkozások és idézések standard szabályait következetesen alkalmaztam, mások által írt részeket a megfelelő idézés nélkül nem használtam fel.

Budapest, 20 22.06.01



a hallgató aláírása

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