Univerza v Mariboru

Fakulteta za kemijo
in kemijsko tehnologijo

Bachelor's Thesis

CELLULOSE-BASED POROUS POLYMERS OBTAINED THROUGHT HIGH INTERNAL PHASE EMULSION

September, 2021

Paula Estévez Recio

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Bachelor's thesis

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Professional title:	Bachelor of Science in Chemical Engineering
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Maribor, 2021

UNIVERSITY OF MARIBOR
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

Place and date: MARIBOR, 02.06.2021

On the basis of Article 330 of the Statute of the University of Maribor (Official Gazette of the Republic of Slovenia, No. 41/2021-UPB13), I issue the following

DECISION ON FINAL WORK

PAULA ESTEVEZ RECIO, student of 1st cycle ABS study programme Izmenjava UN, has satisfied all requirements and is allowed to compose the final work.

The topic of the final work is predominantly from the field of the chair/department/institute:
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Supervisors:

red. prof. dr. PETER KRAJNC, univ. dipl. inž. kem., Supervisor
asist. STANKO KRAMER, mag. kem., Co-supervisor

Title of final work:
Priprava poroznih polimerov na osnovi celuloze z uporabo emulzij z visokim deležem notranje faze

Title of final work in English:
Cellulose - based porous polymers obtained through high internal phase emulsions

The deadline for submission of the final work is 30.09.2021. Final work shall be prepared in line with requirements of the guidelines: *Predloge z navodili za pisanje zaključnega dela* and submitted at the Student Affairs Office. Number of copies: 1. At the same time, a statement from the supervisor is submitted (and possible co-supervisor) on final work adequacy .

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red. prof. dr. Zdravko Kravanja, Dean

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tajnik
red. prof. dr. Zoran NOVAK

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Declaration

I declare that this master's thesis has been made by myself. Any contributions made by others are specifically marked. I have reviewed the literature from the field of the master's thesis using the following keywords:

Source: Science Direct (https://www.sciencedirect.com/)

Keywords:	**Number of references**
PolyHIPE	495
Porous polymers	89
Carboxy Methyl Cellulose	8509
Methylene blue	143932

Source: COBISS+ (https://plus.si.cobiss.net/opac7/bib/search/advanced?db=cobib)

Keywords:	**Number of references**
PolyHIPE	195
Porous polymers	2
Carboxy Methyl Cellulose	20
Adsorption	1933

Total nubmer of articles reviewed: 25
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Maribor, September 2021

Paula Estévez Recio
Signature

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Cellulose-based porous polymers obtained through high internal phase emulsions

Abstract

This thesis aims to explain the synthesis of polyHIPEs containing cellulose. The polyHIPEs were prepared by using oil-in-water (O/W) emulsions. The water (continuous) phase consisted of acrylic acid (AA), carboxy methyl cellulose (CMC), N,N′-methylenebisacrylamid (MBA), a surfactant and appropriate initiators, whereas the oil (internal) phase was toluene. The polymerisation was carried out thermally at 60 ºC for 24 hours. The obtained polymers had a disctint polyHIPE morphology with various diameters, depending on the crosslinking degree and amount of CMC. Interestingly, the presence of CMC and higher crosslinking degree (30 %) caused the formation of bigger pores which essentially formed a material with three levels of porosity – primary, secondary and tertiary. The pore sizes ranged from approximately 32 µm (0 % CMC) to 260 µm (1 % CMC), with the BET surface area ranging from approximately 1.3 m^2/g to 3.9 m^2/g. The polyHIPEs were also used for the adsorption of methylene blue (MB). It was shown that the presence of CMC increased the adsorption of MB, however, at higher concentrations of CMC the adsorption decreased which indicates that an ideal amount of CMC is below 2.5 % (CMC solution).

Keywords: PolyHIPE, acrylic acid, cellulose, adsorption, porosity

UDK: 661.728:665.652.2(043.2)

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Symbols and abbreviations

Symbols

qt	amount of adsorption at time t (mg/g)
MB	mass of dry adsorbent used (gr)
W	Mass of adsorbent (g)

Abbreviations

AA	Acrylic acid
AU	Adsorbance data
APS	Ammonium persulfate
BET	Surface area
CBH	cellulose-based hydrogels
CMC	Carboxy Methyl Cellulose
EA	Elemental analysis
$FTIR$	Fourier Transform Infrared Spectroscopy
$HIPE$	High Internal Phase Emulsion
KPS	Potassium persulphate
MB	Methylene blue
MBA	N,N′-Methylenebisacrylamid
O/W	Oil-in-water
SEM	Scanning Electron Microscopy
W/O	Water-in-oil

1 Introduction

PolyHIPEs are porous emulsion-templated polymers synthesised within high internal phase emulsions (HIPEs). HIPEs are highly viscous, paste-like emulsions in which the major, internal phase, usually defined as constituting more than 74% of the volume, is dispersed within the continuous, minor, external phase [1]. Usually, polyHIPEs are prepared from synthetic monomers which are often not suitable for biological applications, due to their inherent cytotoxicity and non-compatibility with tissues. Given these unfavourable properties, the use of biopolymers, especially polysaccharides, is highly desirable. An example of such a polymer is cellulose. Cellulose is biodegradable and biocompatible which enables its use in personal hygiene products, water reservoirs in agriculture, controlled drug delivery, wound dressing and tissue engineering [2][3]. Therefore, incorporating cellulose into polyHIPEs, which already possess the appropriate porosity and interconnectivity, would be highly favourable in the field of tissue engineering and regenerative medicine [4]. Consequently, the focus of this thesis will be to synthesise cellulose-based polyHIPEs with an open porous morphology.

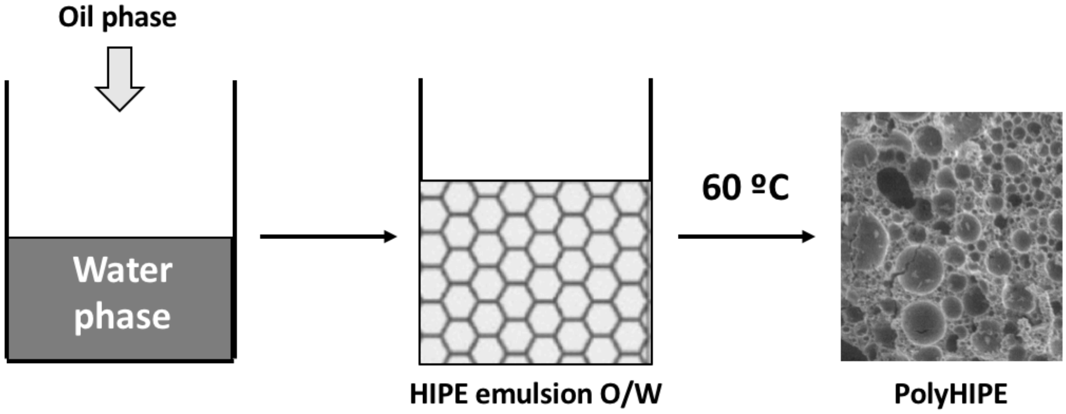

Figure 1-1: PolyHIPE preparation

Materials comprised of cellulose are compatible with living tissues [5]. For the preparation of the polyHIPEs, the aqueous (monomer) phase used is acrylic acid, N,N’-methylenebisacrylamide, carboxy methyl cellulose (CMC), intiators, and an organic phase (toluene).

Because of their high removal effectiveness, such polymers are ideal for the adsorption of remove pollutants from wastewater. The adsorption process utilizing carboxylated cellulose nanofibril-based hydrogels has gotten a lot of interest recently [6]. Given these favourable properties, the synthesized polyHIPEs were used for the removal of methylene blue, a cationic dye, generally used in the textile industry.

2 Theory

Polymers are large molecules made up of smaller molecules (monomers) linked together in practically infinite chain formations by a polymerization process (Figure 2-1). The process of polymerisation is when monomers are linked together by covalent bonds to create a polymer.

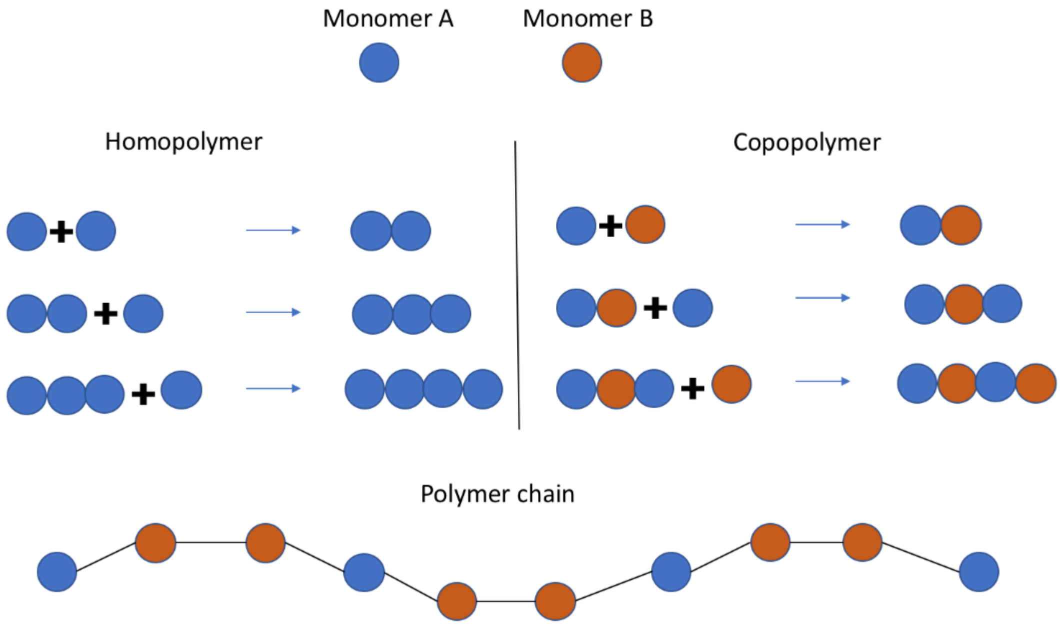

Figure 2-1: Polymerisation diagram

Proteins (polymers of amino acids), nucleic acids (polymers of ribose or deoxyribose sugars with linked purine or pyrimidine bases), and glucose polymers are among the most well-known natural polymers (starch, glycogen, cellulose). Natural polymers were the starting point for synthetic polymers. Cellulose nitrate (Celluloid, 1869) was the first commercially viable synthetic polymer, and it was originally used as a replacement for ivory in billiard balls. Nitration of cellulose, $[C_6H_7O_2(OH)_3]xH_2O$, generates mixes of cellulose trinitrate and cellulose dinitrate, known as guncotton and pyroxylin, respectively. When pyroxylin is combined with camphor, it forms a thermoplastic, which may be molded when heated, according to John Wesley Hyatt. Unfortunately, cellulose nitrate is also a powerful explosive, and its usage in motion picture film and billiard balls has occasionally resulted in spectacular fires. It was quickly superseded by cellulose acetate, which is detailed in the next section [6].
Today's polymers, on the other hand, are primarily semi-synthetic (modified natural polymers) and synthetic (man-made). Polymers are used in a wide range of applications, including coatings, elastomers, adhesives, plastics, fibers, and composites, therefore, the majority of material scientists work on polymer research and development. They also play a vital role in the advancement of biochemistry, molecular biology, and biomedicine [6].
Synthetic chemistry uses a diverse variety of monomers to create synthetic polymers with important physical characteristics (mechanical, thermal, electrical, and optical) (clothing, CDs, toys, etc.). Bakelite (a hard, translucent resin containing phenol and formaldehyde) was developed in 1908 and Parkesite (a combination of nitrocellulose and camphor) in 1856.

2.1 Polysaccharides

Polysaccharides are macromolecules made up of several monosaccharides joined together. They belong to the carbohydrate family and serve a variety of purposes, including energy and structural reserves.

Natural polysaccharides are made up of a large number of monosaccharide residues that are linked together by glycosidic bonds. When these polysaccharides are hydrolyzed, simple sugar units such as glucose, galactose, mannose, arabinose, xylose, and uronic acids are produced. At the cellular level, natural polysaccharides are found as reserve materials in the cytoplasm (e.g., starch) or as structural components of cell membranes and cell walls (e.g., cellulose). Natural polysaccharide extraction, purification, and applications are all influenced by structural features [7].

Natural polysaccharides have a variety of physicochemical properties and functional groups. These also have certain beneficial features such as biocompatibility, biodegradability, nontoxicity, water solubility, stability, greater degrees of swelling, and the ability to be modified chemically, among others [7]. These properties make them great materials for a variety of pharmaceutical and biological applications such as drug delivery and tissue engineering (Figure 2-2). As a result, natural carbohydrates are increasingly being utilized to provide desirable ingredients for specific pharmaceutical purposes [7].

Polysaccharides like hyaluronate, chondroitin, and dermatan sulphates act as lubricants, gels, and compliant matrices in animal tissues, and they also have visoelastic characteristics.

Polysaccharides are suitable molecules for tissue engineering because of their structural and biological roles. Tissue engineering applications require biomaterials with the right biochemical and mechanical characteristics. Biodegradability, biocompatibility, and cell transport capability are all characteristics of polysaccharides as potential biomaterials for tissue engineering.

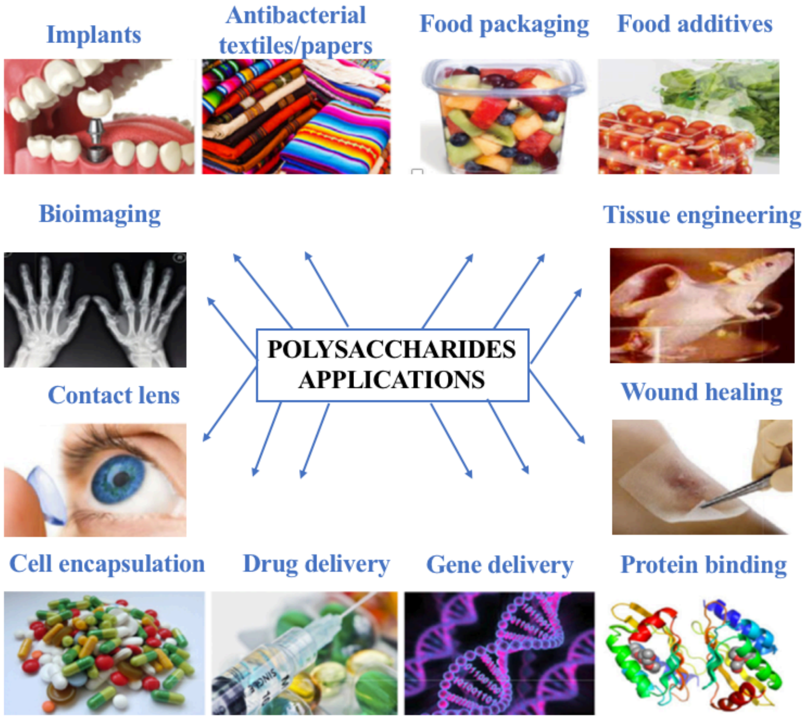

Figure 2-2: Polysaccharides aplications

2.2 Porous Polymers

Porous polymers in the form of monoliths, films, and beads, as in the example in figure 2-3, with well-defined porosities and high specific surface areas are used in a variety of applications (reaction supports, separation membranes, tissue engineering scaffolds, controlled release matrices, responsive and smart materials) and as templates for porous ceramics and porous carbons. The rise in porous polymer system research and development is a relatively new phenomena [8].

They can be categorized as macroporous (pore size > 50 nm), mesoporous (pore size = 2 - 50 nm), or microporous (pore size 2 nm) polymers, depending on the size of the pores [9].

The specific Surface area (the ratio of the area to the mass of the solid) is the characteristic that best characterizes a porous material, second only to pore size. In general, the existence of micropores results in very high specific Surface areas, typically >1000 m^2g^{-1}; however, if the material is microporous, the particular surface areas are smaller, and if the material is macroporous, the specific Surface areas are very low (50 m^2g^{-1}).

Macromolecular design (porous frameworks, stiff structures with intrinsic microporosity), porogen incorporation, phase inversion, and templating are some of the methods that may be utilized to make porous polymers. Block copolymer (BCP) templating, solid particle templating, breath figure templating, and emulsion templating are some of the templating techniques accessible [10].

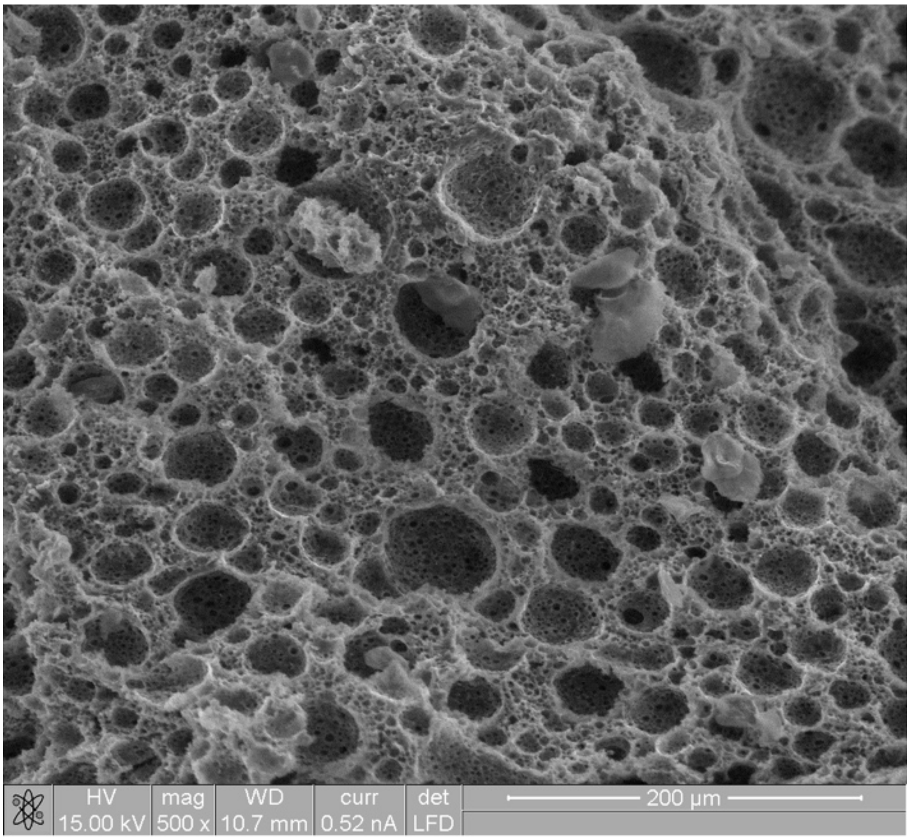

Figure 2-3: Porous polymer

2.3 PolyHIPEs and High Internal Phase Emulsions

PolyHIPEs are porous polymers produced through high internal phase emulsions (HIPEs). HIPEs are very viscous paste-like emulsions, consisting of a consintuous (external) phase and a dispersed (internal) phase. The internal phase generally constitutes at least 74.05 vol. % of the emulsion [8]. With the polymerision of the external phase and the subsequent removal of the internal phase, polyHIPEs are produced, thereby generating a solid material with a linked porous structure [11]. Figure 2-4 shows a schematic example of the thermal polymerization process carried out in this thesis.

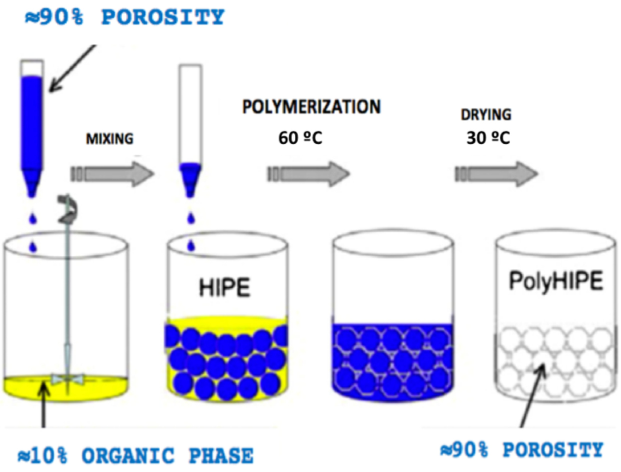

Figure 2-4: A “typical” polyHIPE porous structure with voids and interconnecting holes.

The next image (figure 2-5) shows an example of the structure of a polyHIPE with cellulose obtain in the Scanning Electron Microscopy.

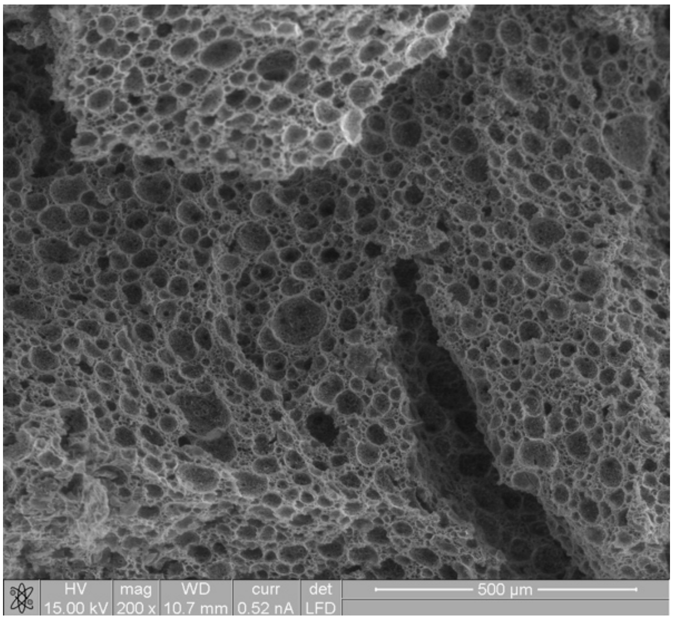

Figure 2-5: A typical porous polyHIPE structure (SEM).

Copolymers, interpenetrating polymer networks, biodegradable polymers, bicontinuous polymers, organic–inorganic hybrids, porous inorganics, and nanocomposites are among the polyHIPE systems developed [8].

Two stages are necessary for the development of HIPE systems. Internal (distributed) phase and continuous (external) phase Water and organic phases are divided into two categories, resulting in two sorts of system:

- W/O (water-in-oil) – the water phase is the internal phase, which is dispersed in the form of droplets in the organic/external phase.
- O/W (oil-in-water) – the organic phase is the internal phase, which is dispersed in the form of droplets in the water/external phase.

2.4 Adsortion with methylene blue

Biopolymer-based hydrogels, such as CBHs (cellulose-based hydrogels), are due to their improved functionality, good solubility in organic solvents, larger surface area, abundance, low cost, better adsorption capacity, biodegradability, ease of fabrication and recycling, and their excellent hydrophilicity a promising adsorbent for wastewater treatment. However, the performance of the adsorbent removing pollutants from wastewater is highly selective for the physical and chemical properties of the adsorbent material [12].

CBHs are usually cellulose derivatives (i.e. natural/pure cellulose and bacterial cellulose), their derivatives (ether derivatives: methyl cellulose, ethyl cellulose, hydroxyethyl methyl cellulose, hydroxypropyl fibre, carboxymethyl cellulose (CMC, etc.)

In this thesis, experiments will be carried out to observe the adsorption of methylene blue (MB). The adsorption of MB on a CBH (synthesized by modification of cellulose and acrylic acid) showed such interaction between electronegative N-atom in MB structure and H atom in –COOH and –OH groups of HG (hydrogels) [12].

3 Experimental section

3.1 Materials and reagents

For the preparation of the emulsions the following chemicals were used:
Monomers:

- Acrylic acid (AA)

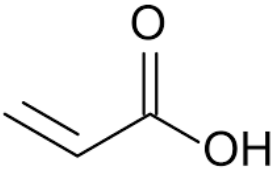

Figure 3-1: Acrylic acid

- Sodium hydroxide
- Carboxy Methyl Cellulose (CMC)

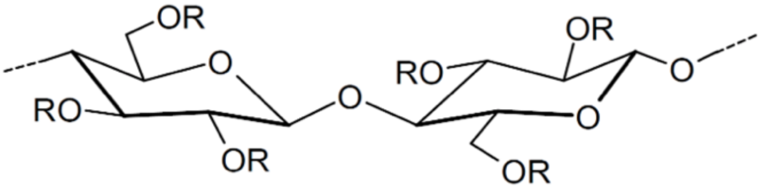

Figure 3-2: Carboxy Methyl Cellulose

Crosslinker:

- N,N′-Methylenebisacrylamid (MBAA)

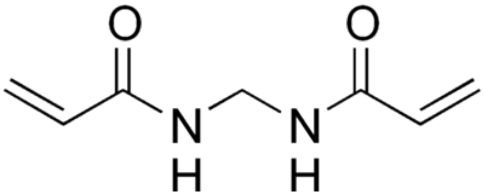

Figure 3-3: N,N'-Methylenebisacrylamid

Surfactant:

- Triton solution X-405 (70%)

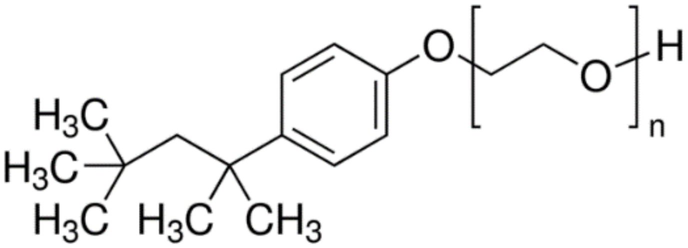

Figure 3-4: Triton

Solvent:

- Toluene

Reducing agent:

- 1,2-Di(dimethylamino)ethane (TEMED)

Initiator:

- Ammonium persulfate (APS)
- Persulfato de potasio (KPS)

3.2 Laboratory equipment

For the preparation and characterisation of the polymers the following equipment has been used:

- Ovearhead Stirrer (IKA)
- Two Neck Round Bottom Flask
- Standard Laboratory Balance
- Conical flaks
- Micropipets
- Beakers
- Heating mantle
- Dropping funnel
- Erlenmeyer flask
- Lab spatula
- Volumetric flask
- TriStar II (Surface Area and Porosity)
- FlowPrep 060 (Sample Degas System)
- Elemental analyser: PerkinElmer EHNS/O 2400 Series II analyzer
- Scanning electron micrscscope: FEI Sirion 400 NC
- UV/VIS: Agilent 8453 UV-Visible spectrophotometer
- FTIR: Shimadzu IRAffinity spectrometer

3.3 Experimental methods

3.3.1 CMC solution preparation

Because of its limited solubility in water, the CMC was dissolved beforehand, enabling the subsequent synthesis of the polymer and eliminating the possibility of the CMC not dissolving entirely. For the preparation of the CMC solutions that will later be used in the reaction to obtain the polyhHIPE, CMC powder and distilled water are needed. The CMC is combined with the distilled water in an Erlenmeyer flask. The mixture is stirred by using a magnetic stirrer to ensure that the CMC is thoroughly dissolved in the distilled water. The mixture was mixed for 24 h on a magnetic stirrer at 45 °C and the CMC solution is prepared and kept at room temperature in the same Erlenmeyer flask. The longer it takes to dissolve the CMC completely, and the more viscous the final combination becomes, the more concentrated the CMC solution is. For this thesis, four CMC solutions are needed (see Table 3-1).

Table 3-1: Prepared CMC solutions.

CMC (%)	CMC (gr)	DISTILLED WATER (gr)
1	1	99
2,5	2,5	97,5
5	5	95
7,5	7,5	92,5

3.3.2 PolyHIPE preparation

Water-in-oil-in-water high internal phase (HIPE) precursors were used to produce porous polymers. Acrylic acid (1.71 g, 23,75 mmol), the crosslinker MBAA (20% and 30%), the surfactant Triton X-405 (2.82 g), various CMC solutions (0 wt. %, 1 wt. %, 2.5 wt. %, 5 wt. % and 7.5 wt. %), sodium hydroxide (0,84 g NaOH) and the initators KPS or APS (6 wt. %) were added to a two neck round bottom flask. The prepared mixture was stirred with an overhead stirrer at 400 rpm for 45 minutes. After 45 minutes toluene (37 mL) has been added dropwise to the monomer solution. After the addition of toluene the mixture was stirred for another 40 minutes. In the case of APS, TEMED (0.10 mL) has been added after the 40 minutes and left to stir for approximately 3 minutes. The obtained emulsion was transferred to a mold and cured at 50 °C for 20 h. The emulsions prepared with KPS were cured at 60 °C for 20 h. The obtained polymers were firstly soaked in methanol and afterward purified with a Soxhlet apparatus for 24 hours using methanol. After the purification the samples were dried under vacuum
Various different polyHIPEs were prepared according to table 3-2.

Table 3-2: Samples with different componets

Sample	**$\%_{MBA}$**	**m_{MBA}(gr)**	**$\%_{CMC}$**	**m_{CMC}(gr)**	**$m_{CMC+H2O}$(gr)**	**m_{NaOH}(gr)**	**m_{KPS}(gr)**
PE19	30	1,21	0	0	7,56	0,86	0,15
PE20.R		1,21	1	0,08	7,64	0,86	0,15
PE21.R		1,21	2,5	0,19	7,75	0,83	0,16
PE22		1,22	5	0,38	7,94	0,84	0,17
PE23		1,25	7,5	0,57	8,13	0,82	0,18
PE25	20	0,81	0	0	7,56	0,85	0,13
PE26		0,81	2,5	0,19	7,75	0,84	0,14
PE27		0,82	5	0,38	7,94	0,84	0,18
PE28		0,83	1	0,08	7,64	0,86	0,14
PE29		0,81	7,5	0,57	8,13	0,84	0,16

3.3.3 Adsortion with methylene blue

Approximately 50 mg of the samples were weighted into a beaker and immersed in 15 mL of methylene blue (MB, 50 mg/L). The samples were left in the MB solution for 24 h. After 24 h the solution was transferred from the beakers by using a pipette, to ensure that none of the polymer particles were transferred with the solution. The adsorption of the solution was measured by using a UV/VIS spectrophotometer ($\lambda = 663$ nm), to determine the the adsorption capabilities of the prepared samples.

3.3.4 Characterisation

Following the synthesis of the polyHIPE and purification with the Soxhlet apparatus, it was characterised using fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), elemental analysis (EA), and surface area (BET).

4 Results and discusion

4.1 PolyHIPE polimers synthesis

Porous polymers with different compositions were synthesized in this thesis. The fabrication of a stable HIPE was the first stage in the synthesis of the porous polymers. The HIPE utilized to make the polymers is an oil-in-water (O/W) emulsion with polymerisable monomers in the continuous phase. Toluene represents the organic phase, whereas acrylic acid, N,N'-methylenebisacrylamide (MBA), CMC, triton x-405 and the initiators make up the dispersed (aqueous) phase.The polymerization was carried out at 60°C and yielded a polyHIPE. The polyHIPEs were prepared using two types of initiators: APS and KPS. Initially, APS was used, however, the polymerization of the HIPE did not produce a stable polymer, as the polymer crumbled into smaller pieces. This was most likely due to a partial polymerization and not a full polymerization. Given the unsuccessful preparation of the polyHIPE by using APS, KPS was used instead with great success.
It should also be noted that the formed polymers are brittle due to the presence of acrylic acid. To evaluate the influence CMC and the crosslinking degree, various CMC concentrations and crosslinking degrees (20% and 30%). Figure 4-1 show samples PE27 and PE23 respectively. a), the polymer after vacuum drying has a white, porous and somewhat brittle appearance. In some of the samples, the polymer easily fell apart, as in b). The porous structure was already somewhat visible with the naked eye, which indicates that the polyHIPE has fairly large pores. This will be discussed in more detail in the morphology section.

Figure 4-1: Sample of the polyHIPE: a) PE27 and b) PE23

4.2 Characterisation

The functional groups, elemental analyses, pore diameter and morphology of the obtained products were determined and detailed in the following sections.

4.3 Fourier-transformifraredspectroscopy (FTIR)

FTIR spectroscopy was carried out to determine to successfulness of the polymerisation.The FTIR measurements were used to determine the presence of certain functional groups in the region between 4000–800 cm^{-1}. The FTIR spectra of PE19 produced by polymerisation without CMC are shown in Figure 4-2. At 1454 cm^{-1}, the characteristic CMC absorption bands develop (C-OH stretching vibrations). Furthermore, the full neutralisation of the carboxyl group arising from AA is strongly connected to the absence of distinctive absorption bands around 3000-2800 cm-1, which are attributed to COOH's C O stretching.
The wide adsorption band between 3600 and 3000 cm^{-1} represents the OH in COOH. Because there are numerous CH_2-CH_2 links, the peaks at 2900 indicate the sp3 CH in the produced polymer. The peak at 1647 cm^{-1} represents the carbonyl group in the polymer; however, it may also be a C=C peak; nevertheless, as these bonds are depleted in this reaction, it is more likely that the peak represents the C=O bonds. The peak at 1550.42cm^{-1} is asymmetric stretching of COO^-, while the one at 1454.33cm^{-1} is the symmetric stretching. The peak at 1114cm^{-1} represents C-O.
Figure 4-3 and figure 4-4 display the FTIR spectra for the CMC containing polyHIPEs. The peak at 3200 is due to the acrylic acid's COOH. Peaks at 1554 and 1400 are most likely the result of asymmetric and symmetric stretching od COO^-.
In conclusion, the most important thing to observe is that we have a clearly visible COOH peak. This means that we have obtained a polyHIPE made up of acrylic acid.

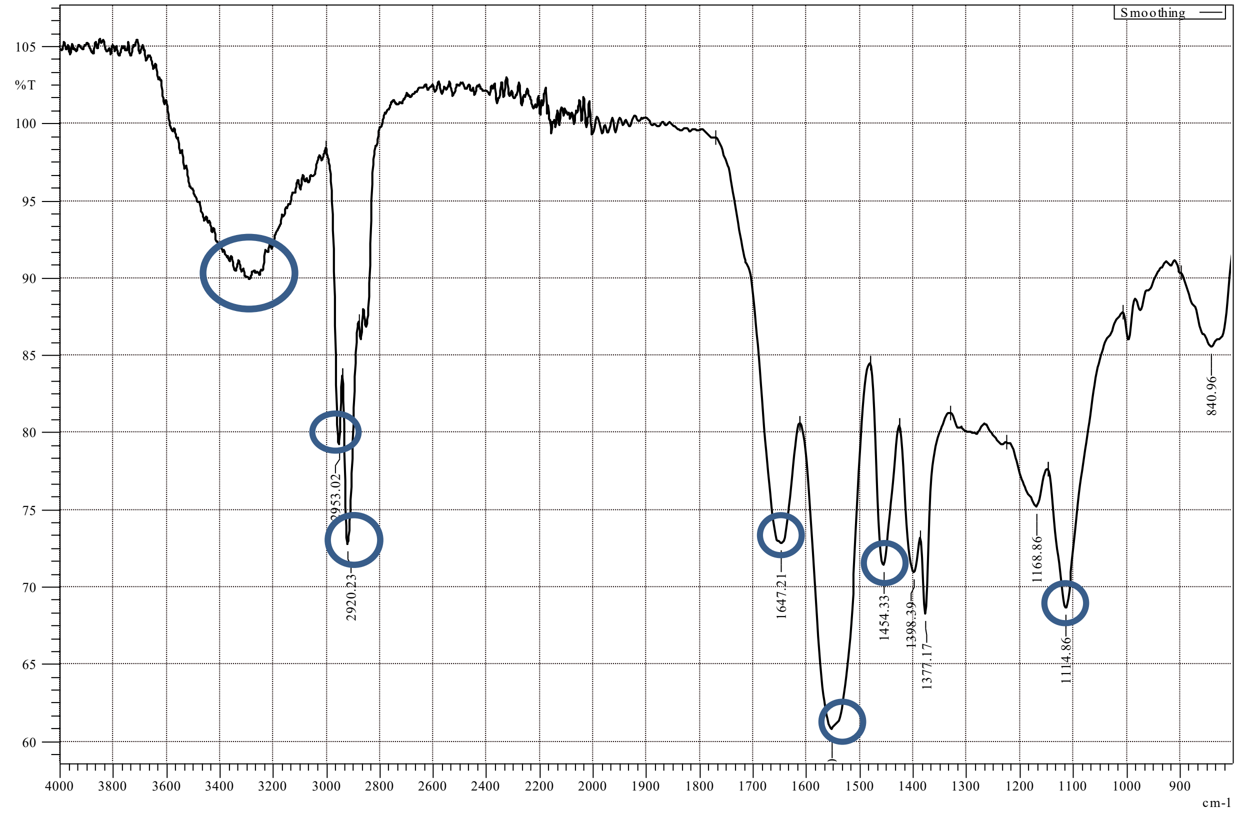

Figure 4-2: FTIR spectra of sample PE19 with the peaks

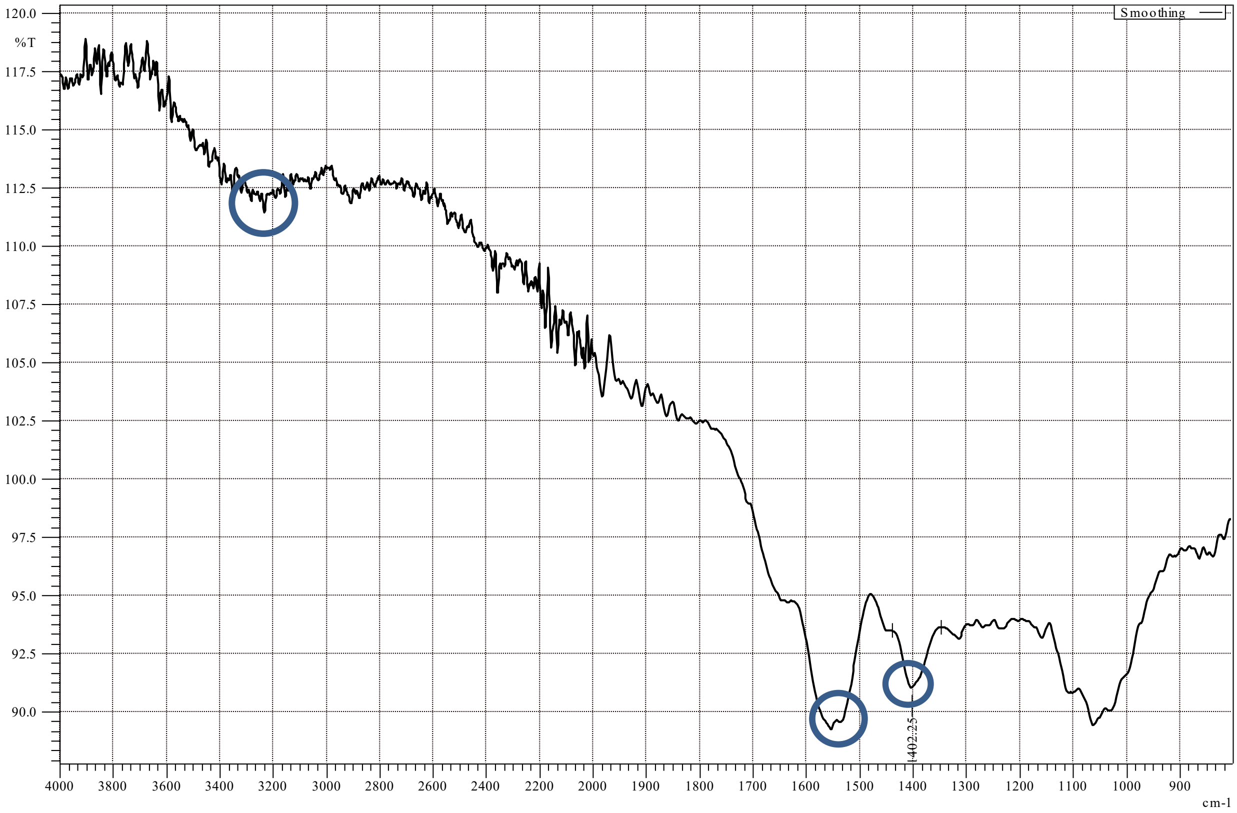

Figure 4-3: FTIR spectra of the PE22

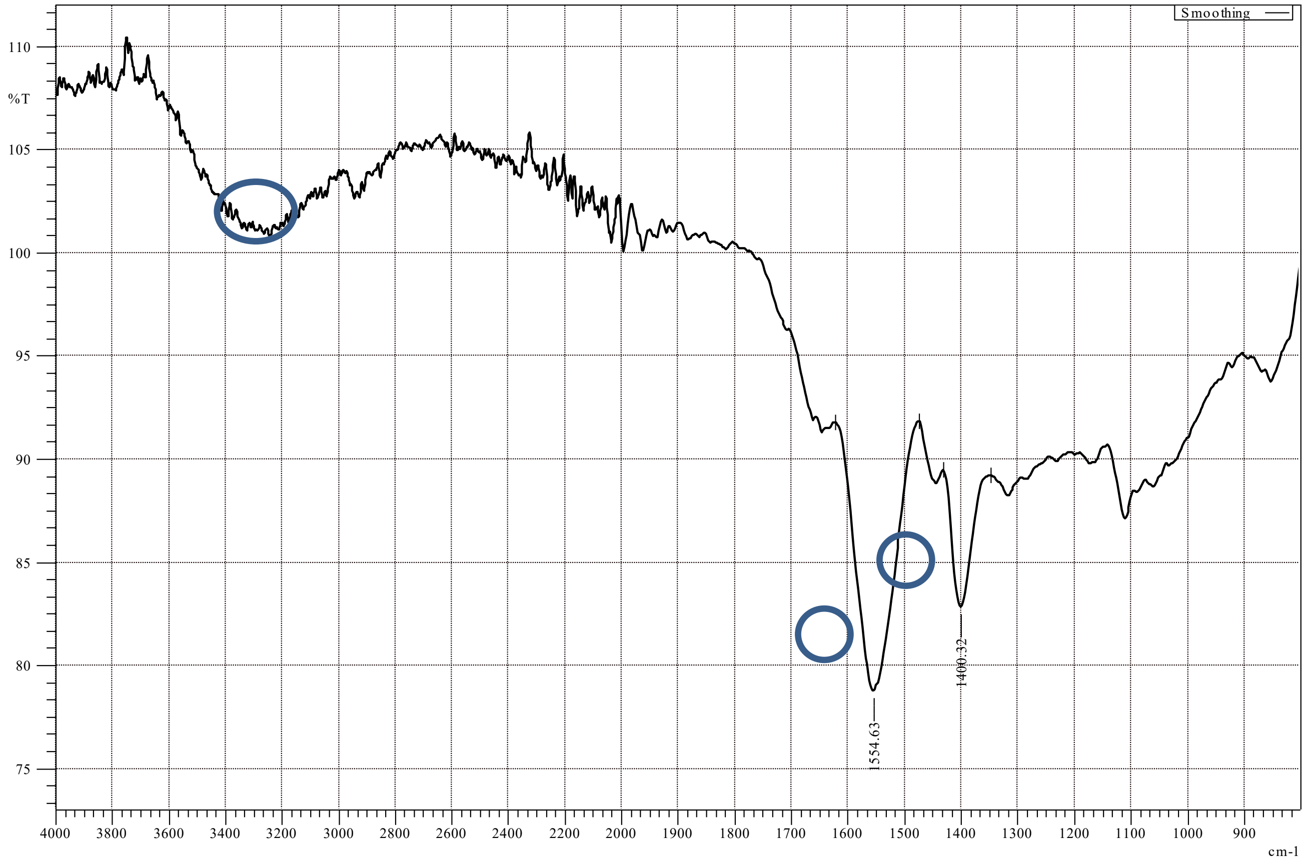

Figure 4-4: FTIR spectra of sample PE26

4.3.1 Elemental analysis

The weight fractions of the elements in the provided samples were determined using elemental analysis. Elemental analysis is performed to evaluate if the polymerisations were successful, and the theoretical values were calculated to find the difference between the theoretical and measured values, as indicated in the preceding section. Table 4-1 shows the findings of the elemental analysis. The calculated and measured values are approximately the same (a maximum of 1% discrepancy between measured and calculated values) which indicates that the polymerization and the formation of the desired polyHIPEs was successful. The analysis mistake might be the cause of the deviations from theoretical values. It needs to be noted that PE22 has the greatest deviation from theoretical values, whereas PE19 has the smallest. This might be related to the inclusion of CMC in the polymer. It is possible that not the entire CMC that had been added to the mixture had reacted during the polymerization, which caused it to be removed during the purification process.

Table 4-1: Calculated (C) and Measured (M) elemental weight fractions of the samples

	C		H		N	
Sample	**C**	**M**	**C**	**M**	**C**	**M**
PE22	34,93%	33,98%	5,99%	5,88%	7,56%	8,46%
PE20.R	35,01%	34,68%	6,01%	6,27%	7,37%	7,75%
PE19	35,33%	35,44%	6,07%	6,44%	6,69%	6,89%

4.3.2 Surface area (BET)

The synthesized polyHIPEs had a considerably low surface area, despite the material's porous and interconnected topology, the voids' comparatively large size results in a low surface area [1]. In the case of the 30 % crosslinked polymers, the sample without any CMC had the highest surface area. This was expected, as the pore size of this sample was the smallest one (Table 4-3). Among the 20 % crosslinked polymers, the sample containing the highest amount of CMC had the highest surface area. This is in accordance with the measured pore diameters as they are the smallest.

Table 4-2: Surface area of the samples

Sample	Surface area (m2/g)
PE19	3,93
PE20.R	1,49
PE21.R	2,69
PE22	2,22
PE23	2,97
PE25	2
PE26	2,38
PE27	1,29
PE28	2,79
PE29	4,87

4.3.3 Morphology

The materials that are made by using high internal phase emulsion templating have a complex morphology consisting of bigger pores known as cavities and smaller interconnecting pores. In addition, a considerably finer porous texture may be produced inside the walls of the base material. There is also a wide range of material sizes, from thin membranes to extremely massive monolithic objects. PolyHIPEs may be utilized in sophisticated material applications that demand careful control of their morphology and characteristics. The morphology can also be changed based with the point of initiation, which has a major impact on the pores[10].

The morphology of the synthesised particles was studied by scanning electron microscopy (SEM). Particle morphology can be affected by several parameters: viscosity, initiation type, initiator weight fraction, surfactant type and weight fraction, stirring speed, monomer types and concentration, as well as other factors. All of the prepared polyHIPEs had an open porous structure. Interestingly, the produced polyHIPEs had only a bimodal porosity in the case of the 30 % crosslinked AA polyHIPE. All the other polyHIPEs had a multi-level porosity consisting of primary, secondary and tertiary pores, as can be seen in Figure 4-5. PE20.R had the biggest pores among all of the prepared samples, while PE19 having the smallest pores among all the prepared samples (Table 4-3). Based on the measured pore diameters it can be seen that the pore diameter decreases by increasing the CMC content in both 20 % and 30 % crosslinked polyHIPEs. This indicates, that the pore diameter can be tailored by increasing the CMC content.

Table 4-3:Pore diameter of the samples

			Pores sizes (µm)		
Samples	Crosslinker	CMC	Primary	Secondary	Tertiary
PE19	30%	0%	-	3 - 5	1 – 2
PE20.R		1%	230 - 270	28 – 40	6 – 8
PE21.R		2.5%	80 - 120	20 – 29	5 – 9
PE22		5%	20 - 50	3 – 8	1 – 2
PE23		7.5%	25 - 53	4 – 7	1 – 3
PE25	20%	0	80 - 110	20 – 30	1 – 5
PE26		2.5%	40 - 80	6 – 15	1 – 6
PE27		5%	20 - 80	5 – 15	2 – 5
PE28		1%	50 - 100	7 – 10	1 – 6
PE29		7,50%	30 - 50	10 - 20	1 – 4

In figure 4-5 the measured pores are shown and the differences between the primary, secondary and tertiary pores are highlighted..

These characteristic large pores appear in these two samples and not in the structure of figure 4-6 (PE19), this may be due to the presence of CMC in the first two samples.

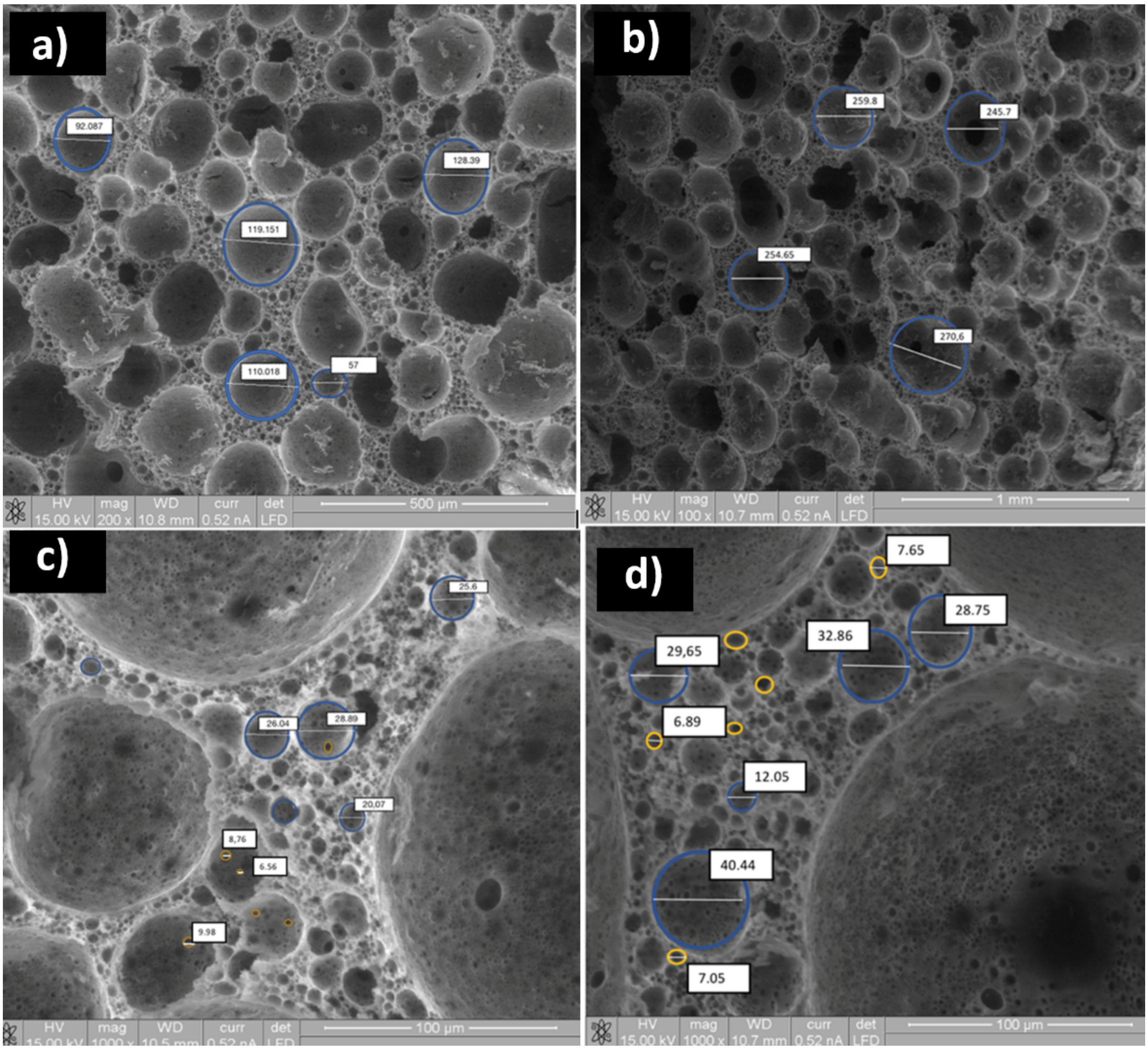

Figure 4-5: Pictures a) and b) show the tertiary pores measured in PE21.R and PE20.R, respectively. Pictures c) and d) show the secondary and tertiary pores measured in PE21.R and PE20.R

Figure 4-6 shows the above-mentioned lack of large pores in the sample without CMC (PE19), with the primary (secondary in the other samples) between 3 and 5 µm and the secondary (tertiary in the other samples) between 1 and 2 µm,

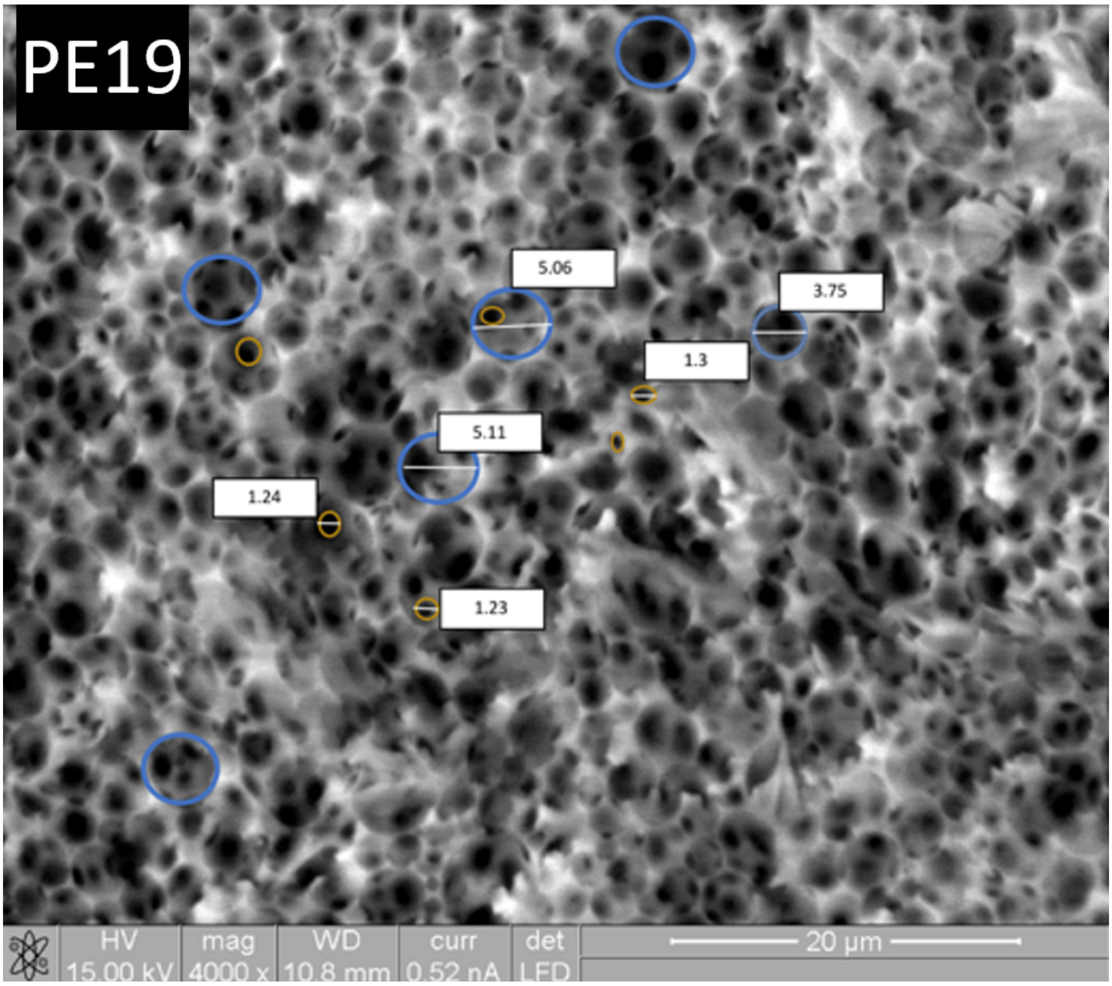

Figure 4-6: The measured pores on the sample PE19

The following figures 4-7 and 4-8, show the difference in the pores between the 30 % and 20 % crosslinked polyHIPEs, respectively; the higher the percentage of crosslinker, the larger the pores and the more homogeneous the appearance of the pores.

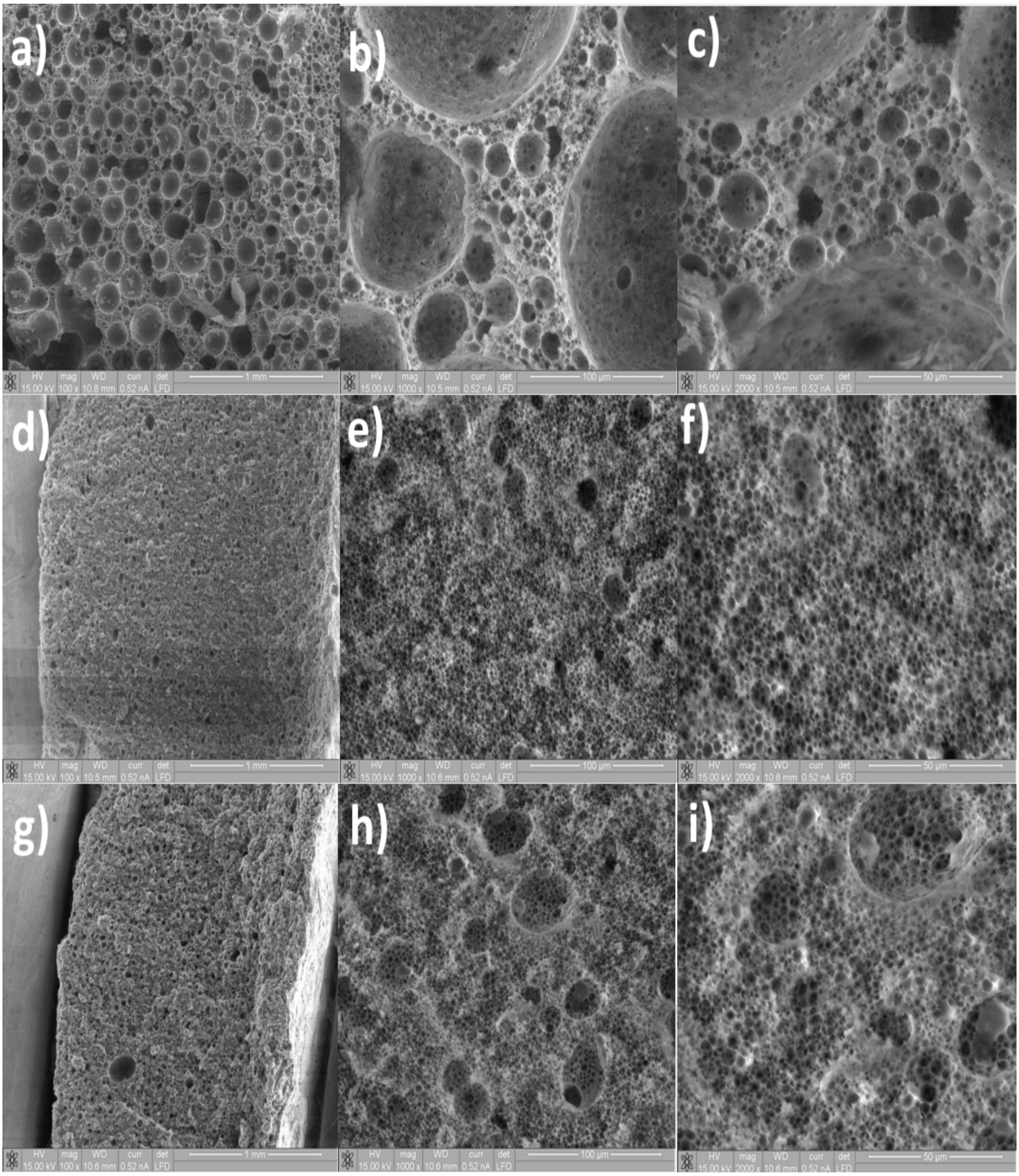

Figure 4-7: Inner structure of: a) PE21 (100 x), b) PE21 (1000 x), c) PE21 (2000 x); d) PE22 (100 x), e) PE22 (1000 x), f) PE22 (2000 x); g) PE23 (100 x), h) PE23 (1000 x), i) PE23 (2000 x)

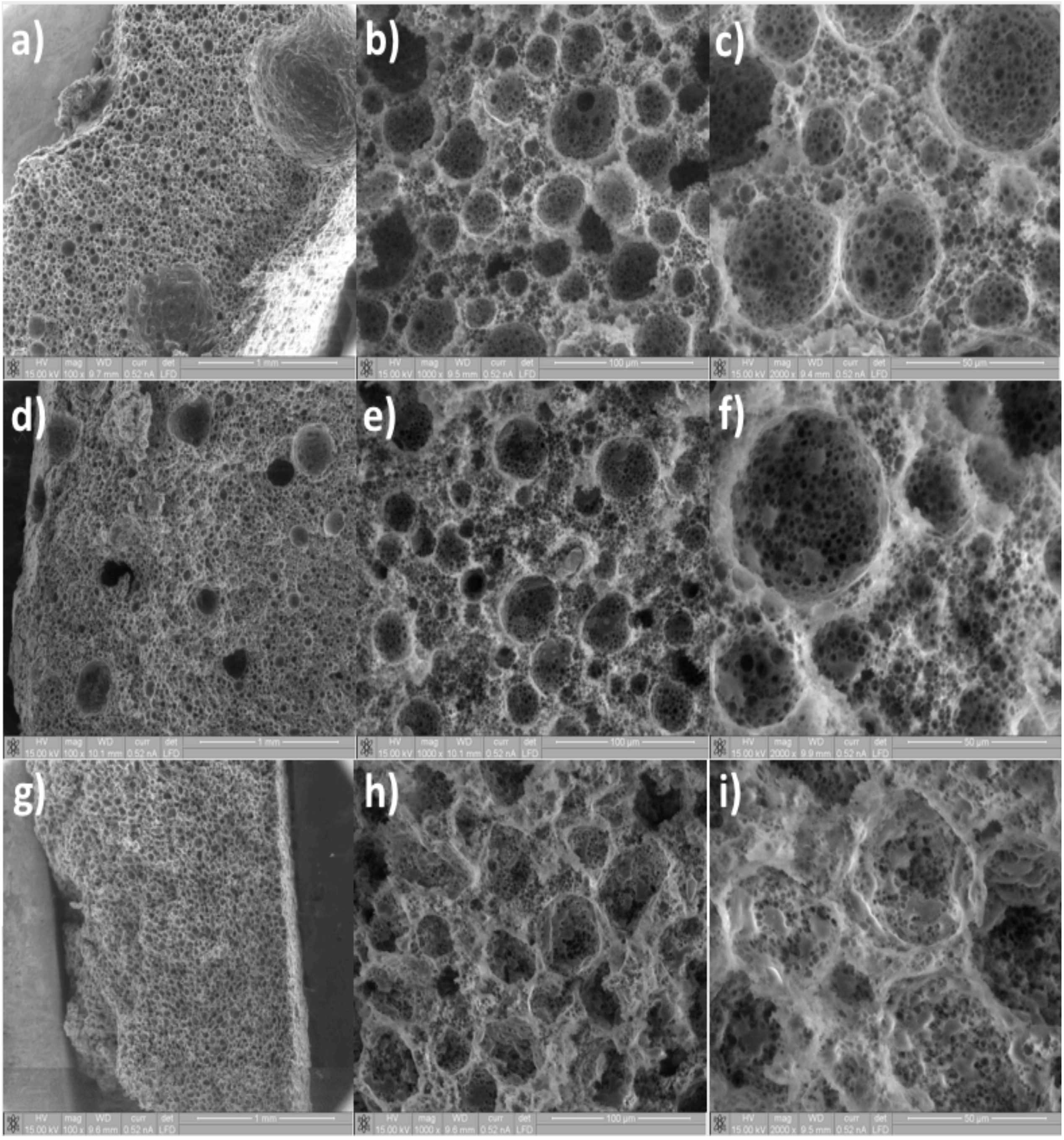

Figure 4-8: Inner structure of: a) PE26 (100 x), b) PE26 (1000 x), c) PE26 (2000 x); d) PE27 (100 x), e) PE27 (1000 x), f) PE27 (2000 x); g) PE29 (100 x), h) PE29 (1000 x), i) PE29 (2000 x)

In figure 4-9 a) and b), the pores are more homogeneous than in the c) and d), which may be due to the absence of CMC in the first one. Pore cavities in the figure 4-10: a) are also more circular than in the polymer where CMC has been added (figure 4-9: c)). In these samples the pores are also open.

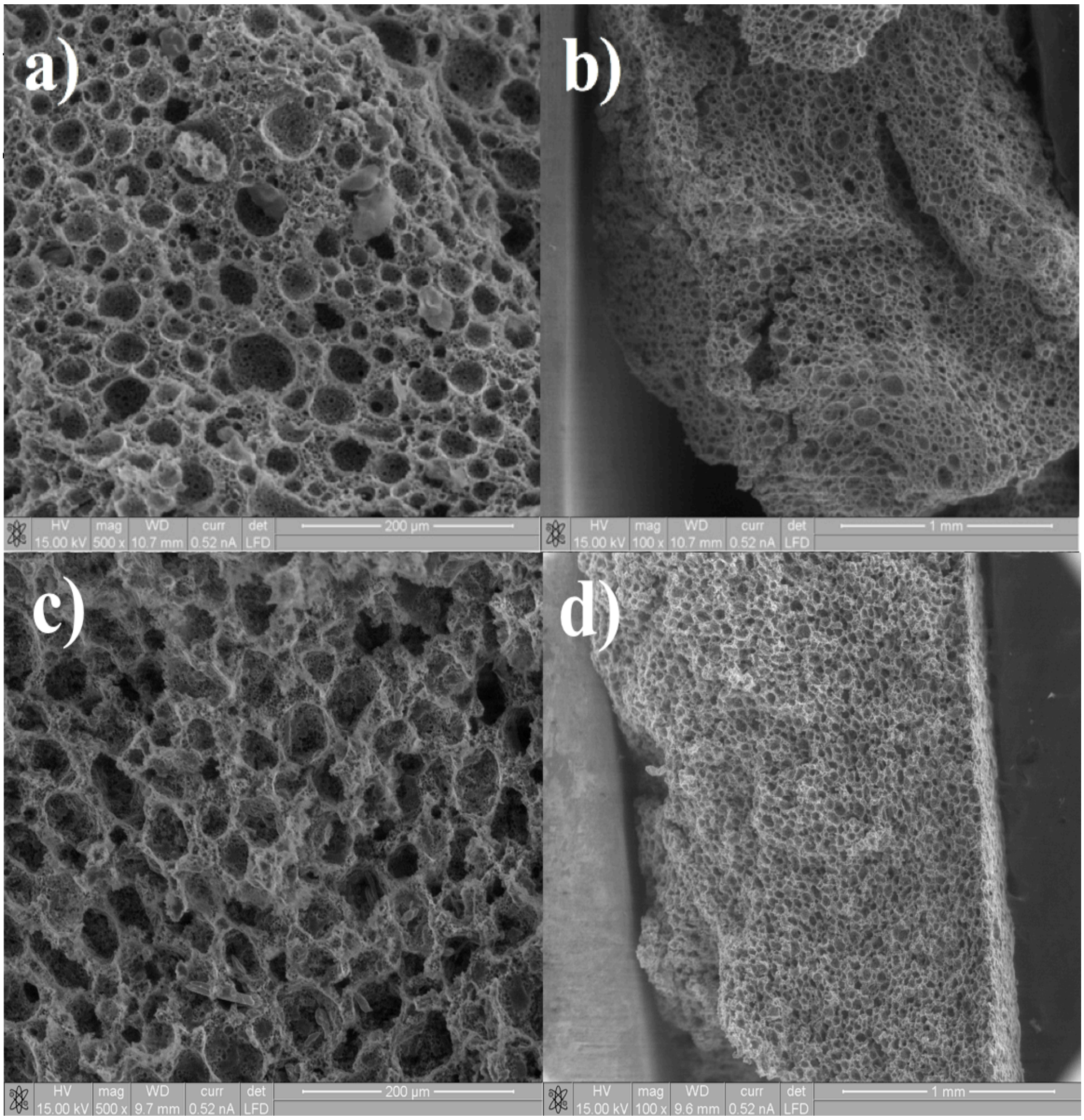

Figure 4-9: Inner structure: a) PE25 (500x magnification),b) PE25 (100x magnification); c) PE29 (500x magnification), d) PE29 (100x magnification)

4.4 Adsortion with methylene blue

Synthetic dyes, such as methylene blue, are an important family of organic chemicals that are frequently found in the environment as a result of their broad industrial usage. Methylene blue is known to cause increased heart rate, vomiting, dizziness, cyanosis and necrosis of exposed tissue, and most of the dyes are known to be mutagenic and/or carcinogenic in the human [13].The contamination of this dye also disturbs aquatic life by preventing the passage of light for the microbiological processes necessary for the balance of the ecosystem to take place[14]. Therefore, it is necessary to remove MB from the environment. Many treatment procedures are utilized for this purpose, with polymer adsorption being one of the most prevalent[15].
Because of the structure of the polymer, which contains functional groups (-OH) from cellulose that tend to create negative dipoles and attract the functional groups of methylene blue that prefer to form positive dipoles, a negative dipole is produced. The dye molecules are maintained on the surface of the biomaterial due to dipole-dipole attractions that occur above or below the polymer structure[16].
For the methylene blue adsorption procedure, the samples were weighted (W) and placed in eakers (approximately 40/50 mg), then a known quantity of the MB solution (15 mL, 50 mg/L) was added and left for 24 hours. Table 4-5 shows the adsorbance data (AU) of the thesis samples.
Table 4-4 shows the data obtained from q_t (amount of adsorption at time t (mg/g)), calculated from the dye concentration at start (c_0(mg/L)) and at the end (c_t(mg/L)) and the volume of solution (V(l)):

$$qt = \frac{(C0-Ct)\cdot V(L)}{W\ (mg)} \qquad \text{(eq. 4.1)}$$

As can be seen in Table 4-4, the samples prepared with the 1 % CMC solution had the highest adsorption. This could be both due to the presence of cellulose and their morphology. It needs to be noted, that the samples prepared with higher CMC contents, namely 5 % and 7.5 % CMC solutions, had lower adsorptions than the ones prepared with 1 % and 2.5 %. This indicates that there's an ideal CMC content that lies between a solution with a CMC content of more than 0 % and less than 5 %.
It should be noted that the adsorption of our polymers increases when a certain amount of CMC is introduced into the process, cellulose improves adsorption. In fact, adsorption will increase as the concentration increases since a strong driving force is created[17].
The polymers had an adsorption ranging from 13,5 to 18,3 mg/g of MB. It was shown that the PE20.R, PE21.R and PE28 polyHIPEs had the highest adsorption, as they adsorbed up to 18.3 mg/g. Interestingly, in the case fo the 30 % crosslinked polymers, PE19 had the lowest adsorption. This might be due to the absence of the multi-level porosity, which is present in the other samples. In the case of the 20 % crosslinked polymers, PE27 and PE29 had the lowest adsorption. This indicates, that the presence of the multi-level porosity increases the adsorption and after a certain CMC content the adsorption gets decreased.

Table 4-4: Amount of adsorbed methylene blue per gram of polymer.

	ct (mg/L)	qt (mg/g)	%CMC
PE19	0,84	14,6	0%
PE20.R	1,50	18,3	1%
PE21.R	0,75	16,1	2.50%
PE22	1,82	16,7	5%
PE23	0,89	15,3	7.50%
PE25	0,92	15,2	0
PE26	0,52	14,0	2.50%
PE27	0,75	13,5	5%
PE28	1,36	17,5	1%
PE29	0,46	13,7	7,50%

In figures 4-10 and 4-11 the different blue colours can be observed according to the amount of adsorbed MB after 24 hours. The decrease of the blue colour is clearly visible in the samples PE20R, PE21, PE22 and PE28, where a higher adsorption has taken place.

Figure 4-10: Samples with methylene blue (PE19 to PE23)

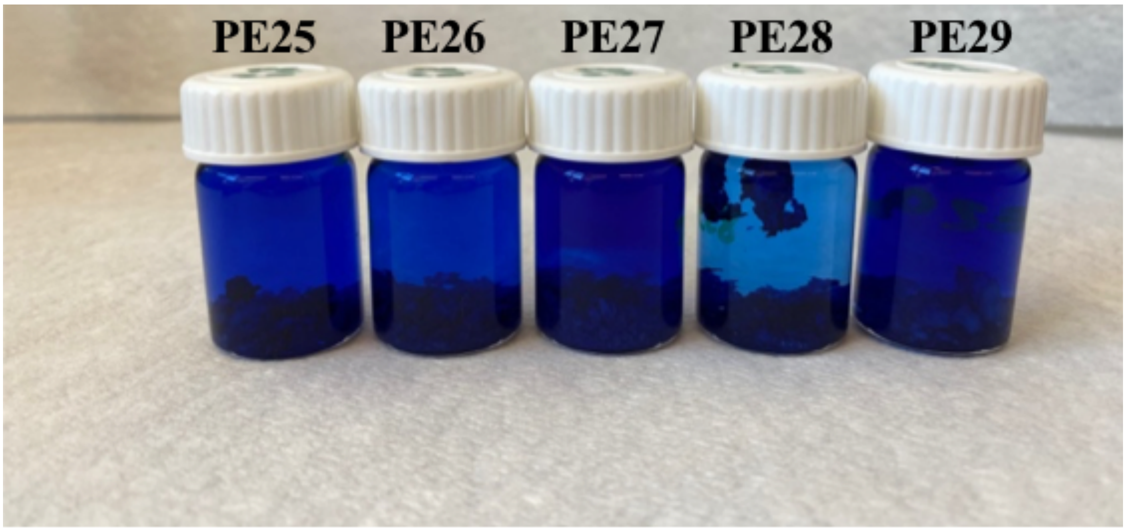

Figure 4-11: Samples with methylene blue (PE25 to PE29)

To measure the adsorption with the UV/VIS, the solution had to be extracted into new canisters in order toremove the polymers. Figures 4-12 show the solutions after adsorption when compared to the 50 mg/L methylene blue solution.The decrease in the intensity of thecolour blue was considerable which also clearly indicated the successfulness of the adsorption visually.

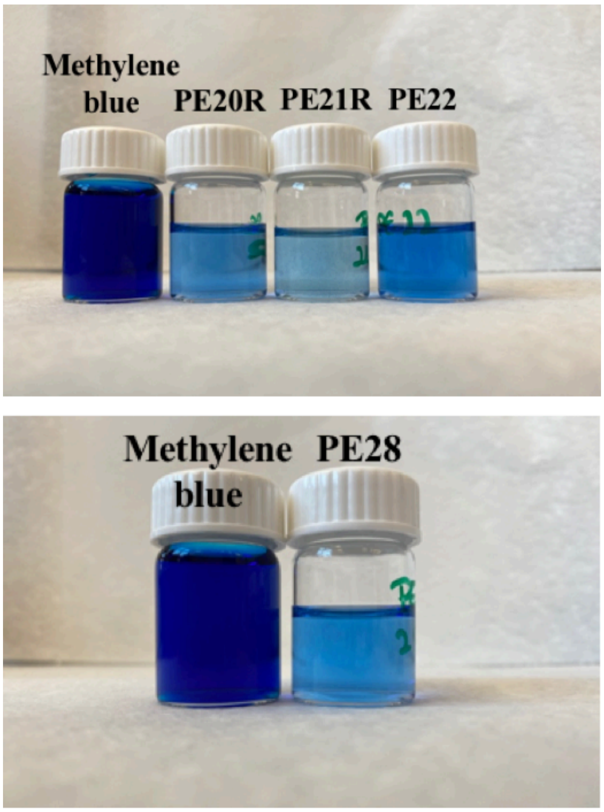

Figure 4-12: Compare the samples (PE20R to PE22 and PE28) with the most adsorption with methylene blue

Figure 4-13 show the polymer after adsorption of methylene blue. This is another proof that the adsorption of the dye was successful, as the polymers had a dark blue colour. The result would have been better if the polymer had not been broken down for further processing, as seen in the figure on the right.

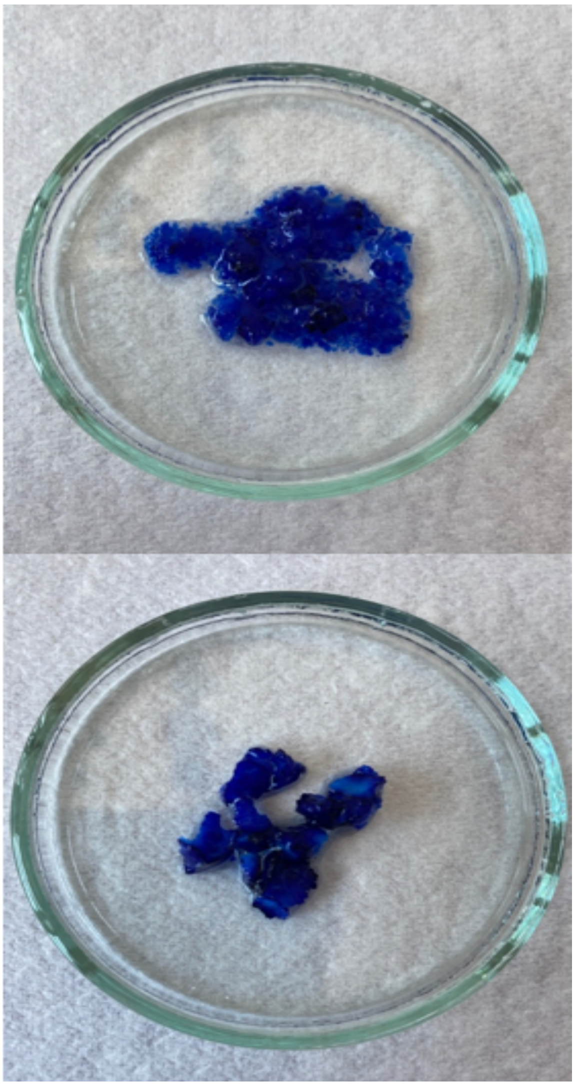

Figure 4-13: The polyHIPE after de adsorption with methylene blue

As we know the adsorption data and that in each sample before introducing the polymer, we have 0.75 gr of methylene blue, table 4-5 shows the amount of methylene adsorbed by our polymer in each sample. The adsorption percentage is between 81% and 98%. In some cases, almost 100% is reached, as for example in PE21.R, PE28 and PE20. These adsorptions compare well to other adsorption experiments where the adsorption is similar to that of our samples [18].

Table 4-5: Methylene absorbed by each polymer sample

	MB (gr)/ Polymer (gr)	**Polymer (gr)**	**Adsorbed MB (gr)**	**% Adsorbed**
PE19	14,6	0,043	0,62	83,14
PE20.R	18,3	0,039	0,73	96,99
PE21.R	16,1	0,046	0,74	98,50
PE22	16,7	0,043	0,72	96,36
PE23	15,3	0,04	0,62	82,27
PE25	15,2	0,04	0,62	81,58
PE26	14	0,048	0,67	89,68
PE27	13,5	0,047	0,64	85,03
PE28	17,5	0,041	0,73	97,27
PE29	13,7	0,049	0,68	90,79

5 Conclusion

This thesis showed the ability to synthesise cellulose containg porous polymes through high internal phase emulsion templating. The polymers were produced by combining acrylic acid, N,N′-nethylenebisacrylamide and carboxymethyl cellulose. Polymers with various CMC fractions and two crosslinking degrees (20 % and 30 %) were prepared. The polymers were shown to have a multi-level porosity and an open porous morphology. The diameters of the primary pores ranged up to 270 µm, for the secondary pores up to 40 µm, and for the tertiary pores up to 9 µm. It was shown that both the CMC content and the crosslinking degree affected the pore diameter. The higher the CMC content, the lower the pore diameter and the higher the crosslinking degree, the bigger the pore diameter. The polyHIPEs were shown to have a specific surface area ranging from 1.29 to 4.87 m^2/g, with the 30 % crosslinked non-CMC containg polyHIPE having the biggest surface area. This was most likely due to the pore size which was considerably smaller. Lastly, the adsorption capabilities of these polymers were evaluated by using methylene blue. The polymers adsorbed from 13.5 to 18.3 mg/g methylene blue, with clearly higher adsorptions when adding a certain amount of CMC.

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7 Suplementary information

7.1 PolyHIPEpolimerssynthesis

For the calculation of the grams needed for the polymers, equation X is used with a crosslinker percentage of 10% and 20%, a molecular mass of acrylic acid of 72.62 g/mol and of MBA of 154.17 g/mol.

$$\%\,crosslinker = \frac{moles\ MBA}{moles\ MBA + moles\ AA}$$

$$mass\ MBA\ (g) = \frac{\frac{mass\ AA\ (g)}{Mm\ AA\left(\frac{g}{mol}\right)} \cdot \frac{\%\,crosslinker}{100}}{0{,}9 \cdot Mm\ MBA\ (\frac{g}{mol})}$$