Research Article

Swelling Properties of Biodegradable Superabsorbent Polymers

Elżbieta Czarnecka[*] , **Jacek Nowaczyk**

Faculty of Chemistry, Nicolaus Copernicus University, 87-100 Toruń, Poland
E-mail: elzbieta.czarnecka@tzmo-global.com

Abstract: The size of the global market for biodegradable superabsorbent materials has been estimated at USD 120.64 billion. It is expected to register Compound Annual Growth Rate (CAGR) at 6.2% in 2018-2025. Superabsorbent polymers (SAP) are most frequently used in the hygiene products industry in the form of non-biodegradable poly (sodium acrylate). Most personal care products end up in landfills where decomposition times are estimated to be up to half a thousand years due to the synthetic polymers. Simple replacement of poly (sodium acrylate) with biodegradable superabsorbent polymer is a challenging task that includes several stages of scientific investigation. In this paper, the sorption of water and electrolyte solutions are discussed. Biodegradable superabsorbent polymers were obtained from polysaccharides, while a proportionally varying amount of the cross-linking agent was used. The absorption properties of deionized water and sodium salt solution were tested and the influence of polymer drying was discussed. The superabsorbent polymers were dried as follows: dM1-the sample was frozen at -20°C for 48 hours and was dried in vacuum (10^{-2} Tr) at room temperature for 48 hours; dM2-the sample frozen to -200°C for 2 hours and was vacuum (10^{-2} Tr) dried at room temperature for 48 hours; dM3-the sample was dried in a vacuum dryer (~10 Tr) at 50°C for 24 hours, dM4-the sample was frozen to -80°C for 24 hours and then freeze dried for 78 hours.

Keywords: biodegradable superabsorbent polymer, swelling properties, sodium chloride solution, distilled water

1. Introduction

The size of the global market for biodegradable superabsorbent materials has been estimated at USD 120.64 billion. It is expected to register CAGR at 6.2% in 2018-2025.[1] The increase in demand for disposable diapers, incontinence products for adults and hygiene products for women is expected to fuels the development.[2]

Superabsorbent polymer (SAP) is a special class of polymers with three-dimensional hydrophilic networks that retain and absorb large amounts of aqueous solution or water. While the swelling or absorption capacity of hydrogels in water is less than 100% (1 g/g), SAP can absorb much larger amounts of water from 1000 to even 100000% (10-1000 g/g).[3] Superabsorbent materials are one of the key products used in the production of baby diapers. Poly (itaconic acid), polysaccharides, polyacrylamide and poly (vinyl alcohol) are the main product segments because they have excellent absorption rates and biocompatibility as well as easy degradation. Usually, when polymers are removed in the wild, they remain degraded for a long time. One solution to this polymer problem after use is to develop biodegradable polymers. Biodegradable polymers can ultimately be biodegradable by microorganisms in the natural environment to carbon

dioxide (CO_2) and water (H_2O). Various types of biodegradable plastics have been developed.[4]

The swollen superabsorbent polymer is considered to be in thermodynamic equilibrium with its environment. The important factor defining its efficiency is the capacity of the polymer network to contain the external solution. This feature is directly related to the equilibrium degree of swelling. In the swelling abilities of polymer networks crucial role play topological barriers such as cross-links, branches, and crystallites present in the network. The density of these barriers influences the swelling properties on one hand and the diffusion coefficients of solute components on the other. It is common knowledge now, that the equilibrium degree of swelling of the polymer network decreases as the cross-linking density increases. This is accompanied by a decrease in the value of apparent diffusion coefficients in the system. In other words, increasing the cross-linking density will decrease both the solute capacity of the superabsorbent polymer and the swelling rate.

The aim of the recent study concerns the investigation of the physical properties of biodegradable superabsorbent polymer related to different post-synthesis treatment. In general, obtained through synthesis the polymer was exactly the same but it occurred that a simple process such as drying can highly influence the swelling properties of the end product. In this context, four different drying techniques have been applied. In the following, the reader will find the detailed description of drying applied to polymers consisting of polysaccharides cross-linked with natural crosslinker.

Recently, much emphasis has been placed on reducing the amount of production and the impact of synthetic polymers on the natural environment. Many laws have been introduced to reduce carbon dioxide emissions into the atmosphere, which is to force entrepreneurs to change their sustainable development policy. Hygienic products consist of a comfortable, flexible and thin layer of various types of synthetic polymers at the expense of biodegradable properties. The products are becoming thinner due to the use of poly (sodium acrylate). In the article, we investigate the swelling properties of a biodegradable and natural polymer-based alternative to synthetic superabsorbent polymers. The replacement of synthetic polymers in this application seems inevitable to reduce the environmental impact of hygiene products.

2. Research methodology

The detailed description of biodegradable superabsorbent polymers synthesis is recently encrypted and can't be given in full detail. In the course of this study, four SAP polymers based on polysaccharide molecular skeleton were obtained from starch (St) and chitosan (Ch) substrates. The polymers differ in the content of the biobased crosslinker used in the synthesis. As a reference material, interpenetrating network (IPN) hydrogel of Ch and St without crosslinker was taken as (Polymers E). The polymer samples denoted with consecutive capital letters A to D represent polymers with different crosslinker content explained in Table 1. The effectiveness of crosslinking was studied by means of IR spectroscopy. Crosslinking bridges give a unique new band at about 1700 cm^{-1}.[5] The band is not present in the Polymer E spectra and its intensity increases with the crosslinking degree. It is shown in Figure 1 and selected data are gathered in Table 1.

Table 1. Description of investigated polymer samples

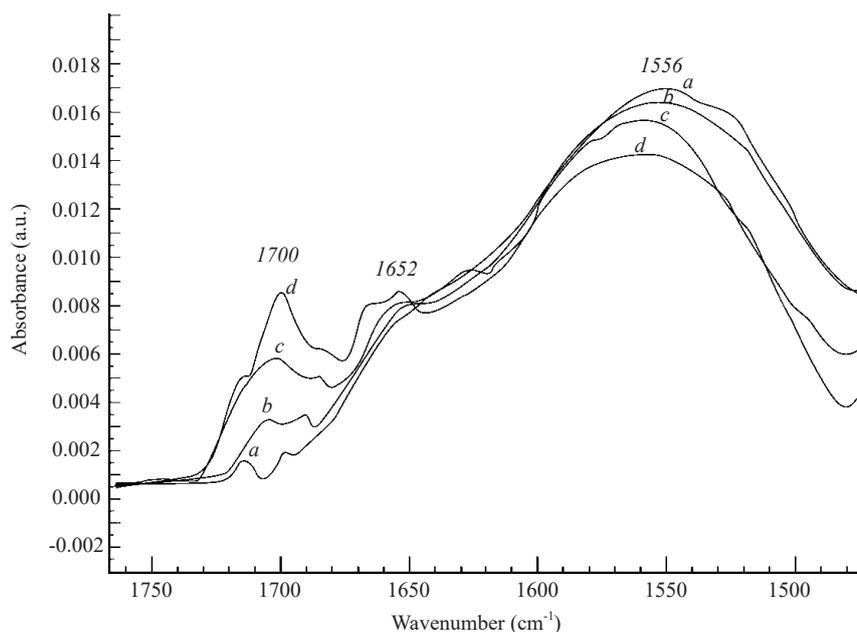| Sample code	Amount of crosslinker (g per g of polymer)	Location of $v_{(CO-NH)}$ band (cm^{-1})	Intensity of $v_{(CO-NH)}$ band (a.u.)
A	0.02	1715	0.0016
B	0.03	1705	0.0034
C	0.04	1702	0.0058
D	0.05	1700	0.0085
E	0.00	-	-

Figure 1. FTIR spectra of polymer samples obtained with different amount of crosslinking agent: 2% (a), 3% (b), 4% (c) and 5% (d)

Polymers were synthesized in aqueous solution and then precipitated from reaction mixture with acetone, followed by rinsing with deionized water and then ethyl alcohol. The resulting material was split into four batches and introduced to four different drying routes. In the first drying method (abbreviated as dM1) the sample was placed in a freezer and kept at -20°C for 48 hours, then transferred to a vacuum chamber under pressure 10^{-2} Tr where it was left to dry over $CaCl_2$ at room temperature for 48 hours. The second method (dM2) was similar to the first except the sample was frozen using liquid nitrogen and transferred to a vacuum chamber directly from the nitrogen bath. In the third method (dM3) a sample liberated from the reacting mixture after purification was dried in a vacuum dryer (p = 10 Tr) at 50°C for 24 hours. In the fourth method (dM4) the sample was frozen to -80°C for 24 hours and then placed in a freeze dryer for 78 hours.

Samples of the synthesized polymer material were structurally identified by means of Fourier transformation infrared spectroscopy (FTIR). In the recorded spectra, specific bands reflecting the degree of crosslinking were found. The fragment of IR spectra, showing the region of most significant changes caused by the crosslinker is shown in Figure 1. The spectra for the intensity considerations were standardized taking the band at 1371 cm^{-1} corresponding to amine-like C-N stretching vibrations overlapping with CH_3 symmetrical deformations (1370 and 1430 cm^{-1}) that do not undergo changes during synthesis.[5]

The swelling was studied by means of absorption of water and aqueous 0.9% wt. NaCl solution. Polymer samples that were dried using different methods were tested using the "Tea-bag method". For the swelling test, bags were produced from two 70 × 150 mm sheets of a 270-mesh tissue paper. The bags before use were stored in a desiccator under silica gel. For the absorption test, a polymer sample (0.1000 ± 0.01 g), stored after drying in a desiccator under silica gel for at least 10 days, was closed inside the bag sealed along the fourth edge. The bag containing the sample was weighed and then placed in the testing liquid (H_2O or NaCl solution) for 24 hours. Afterwards, the bag was removed from the liquid, it was allowed to hang for about 0.5 min and then placed on a piece of filtrating paper to remove the excess liquid before being weighed again.[6] The liquid absorption was calculated as equilibrium sorption capacity (ESC) defined by mass of liquid in grams per 1 g of dry polymer according to the equation:

$$ESC\ [g\,/\,g] = \frac{W_i - W_e - W_d}{W_d}$$

where: W_i is the weight of the wet sample and bag, W_e is the weight of the dry bag, and W_d is the weight of the dry polymer sample obtained by the given drying method.

3. Results and discussion

Samples A to D shown to be superabsorbent samples, where the content of the cross-linking agent increases proportionally, while sample E is reference non-crosslinked hydrogel. Actually, sample E consists of a mixture of two bio-based hydrogels crosslinked physically by intermolecular interactions and chains entangling. The swelling behavior of a superabsorbent polymer is influenced by various factors, such as the presence of hydrophilic group, the elasticity of polymer network, the size, the nature of polymer network, crosslinking density, the composition of the absorbent, the surface area and pH and temperature of the swelling medium.[7] Crosslinking is necessary to form a superabsorbent polymer in an aqueous environment and to prevent the breakdown of the hydrophilic polymer chains. According to the data in Table 1, crosslinker concentration in synthetic mixture corresponds to a degree of crosslinking in the resulting polymer. The influence of crosslinking degree on the water absorbency expressed as ESC was examined in the context of different drying techniques. As it could be foreseen, the increase in the crosslinking degree causes the drop of ESC in all studied samples. The trend is seen in the data collected in Table 2. The increase of crosslinking degree leads to a decrease of the volume of free space between the polymer chains[8] and, in consequence, less solvent can be contained in the polymer matrix. On the other hand, sample E composed of the mixture polymer chains that are not bounded by crosslinker shows the lowest ESC which seems to be in contrary to the expected trend.[7,9] However, sample E contains physical kinds of crosslinks, which although weaker occur more frequently along the chains. In consequence, the material in sample E has different swelling characteristics.

Table 2. Water equilibrium sorption capacity (ESC)

Sample		ESC in water [g/g]				
Characteristics		A	B	C	D	E
Frozen to -20°C and vacuum (10^{-2} Tr) dried	dM1	121.9	73.3	116.9	68.1	32.6
dried in a vacuum oven	dM2	121.9	119.6	112.0	105.6	51.5
Frozen to -200°C and a vacuum (10^{-2} Tr) dried	dM3	214.0	212.6	210.1	208.3	158.9
Dried in a freeze dryer at -80°C	dM4	251.4	235.7	204.9	196.4	99.9

The data in Table 2 can be interpreted in the context of gel chemistry. In the case of non-crosslinked material, the structure of the polymeric chains is loose and does not support stable solute absorbency. Binding chains in a more compact structure triggers the gel formation ability and so the solute absorbency. This ability increases with stabilization of the structure by crosslink bridges, however at some point further crosslinking results in decrease in space available for solute in polymers 3D matrix.

Another aspect, crucial for the aim of this study is the influence of post-reaction treatment on solute absorbency. In the case of water ESC, the smallest values were found for the dM1 method, the values are close to those obtained for method dM2 in common vaccum dryer and vaccum oven. Apparently, freezing the samples with liquid nitrogen (dM3) or dry ice (dM4) yield significantly higher ESC characteristics.

Looking for a relevant superabsorbent polymer for industry (agriculture, hygiene products), it is necessary to investigate the absorption properties not only in pure water but also in salt solutions. Ions present in the electrolyte solution interact with the ionogenic groups in the polymer backbone and this has a significant impact on the swelling properties. In our study, we have investigated the swelling of studied superabsorbent polymers in solution mimicking body fluids (0.9% NaCl solution), the results are shown in Table 3.

A screening effect of the additional cations from the salt solutions caused a non-efficient anion-anion electrostatic repulsion. This led to the reduction of the osmotic pressure difference between the hydrogel network and the external solution.[10,11] And then, the decreasing swelling driving force induced a decrease in the water absorbency. The combination of additional effects including osmotic pressure and ionic interactions inside the SAP cavities disturb

the unequivocal relationship between the degree of crosslinking and 0.9% $NaCl_{aq}$ ESC. A general conclusion can be drawn from the data in Table 3 is that the highest ESC values reveal samples dried in a vacuum freeze dryer (dM4). This method makes it possible to increase the space availability for solvent particles and the contact area between the polymer layer and the solvent which causes the swelling of the polymer chains. The materials dried in a vacuum dryer shows the lowest ESC values, which may be caused by treatment in elevated temperature (50°C). This conclusion corresponds with the observations of the characteristics of water absorbency. It can be explained by the fact that deep freezing of the polymer after synthesis results in the formation of ice microcrystals in the polymer network. When ice is evaporated by sublimation in vacuum the material preserves the cavities formed by ice crystals and is capable of containing more solute in the gel (higher ESC). On the contrary, then the water present in the polymer matrix evaporates while in liquid state, it gradually decreases the volume of liquid clusters and cavities filled with it continuously subside. Consequently, the polymer chains approach and more inter-chain interactions may build up physical crosslinking that is further difficult to break by subsequent water sorption. Comparing our finding to corresponding results obtained for purely synthetic polymers it noteworthy to mention the data published by Castrillon N., Echeverria M., Fu H. et al.[12] In the case of "Sodium polyacrylate", they have obtained ESC from 100 to 1000 $g \cdot g^{-1}$ of deionized water absorption. On the other hand, for "Gellan gum with Jeffamine", a value of 77 to 145 $g \cdot g^{-1}$ was achieved for deionized water, while for "PGA with L-lysine" deionized water absorption was in the range from 900 to 2750 $g \cdot g^{-1}$. These are polymers that could be used in hygiene products, i.e. the industry that interests us the most. Guan H., Li J., Zhang B. et al.[13] developed a biodegradable polymer containing cellulose, acrylic acid and acrylamide as monomers, Span-80 as a dispersant and potassium persulfate as initiator. The maximum absorption rate for salt water and water reached 72.48 $g \cdot g^{-1}$ and 706.14 $g \cdot g^{-1}$, respectively. After modification with various cross-linking agents, the superabsorbent polymer achieved higher water absorption results ranging from 836 to 903 $g \cdot g^{-1}$. Referring to the publications of other scientists and their data on the absorption properties of their superabsorbent polymers, it can be seen that the results of the swelling properties of our polymer samples are rather typical for bio-based superabsorbent polymers.

Table 3. Electrolyte solution equilibrium sorption capacity (ESC)

Sample Characteristics		ESC in 0.9% $NaCl_{aq}$ [g/g]				
		A	B	C	D	E
Frozen to -20°C and vacuum (10^{-2} Tr) dried	dM1	34.7	34.3	29.5	28.7	25.4
dried in a vacuum oven	dM2	21.6	205.4	19.9	184.6	12.3
Frozen to -200°C and a vacuum (10^{-2} Tr) dried	dM3	34.8	32.5	29.9	274.5	18.6
Dried in a freeze dryer at -80°C	dM4	45.9	432.1	409.5	395.5	28.6

The material porosity and the swelling capacity are not always directly correlated with each other; however, the microarchitecture of the porous network can play a significant role in controlling water sorption by the superabsorbent polymer.[14] Increasing the number and size of the pores increases the volume of the absorbed liquid (Figure 2). It also depends on the number of interconnections of individual channels and the shape of the pores. The maximum degree of swelling for cross-linked hydrogels is obtained in deionized water, since increasing the ionic strength of a solution minimizes the repulsion between functional groups by screening negative charges. The degree of swelling is significantly reduced in presence of salts. A less porous scaffold would present a lower swelling ratio.[15,16] It can be concluded that the samples prepared without the use of vacuum were compact, hard, without microporosity, while those in which a vacuum dryer or freeze dryer was used were characterized by increased volume, lightness, "meringue" structure and high porosity.

The adsorption process takes place on the adsorbent/adsorbate surface and the interactions between the components are complex processes through ion exchange and chelation between ionized and non-ionized functional groups of the

superabsorbent and positively charged metal ions.[17] Before reaching equilibrium conditions, adsorption takes place in three stages: external diffusion, intramolecular diffusion and adsorption. In order to determine the predominant adsorption step, an intramolecular diffusion model can be used to describe the adsorption process. In kinetic studies, the sorption of metal ions in hydrogels follows a pseudo-second order model, which indicates that chemical sorption is the rate controlling step.[18] Chemical sorption is characterized by valence forces resulting from the sharing and exchange of electrons between the superabsorbent and metal cations. Ions with a larger radius of ions generate more electrostatic interactions with adsorbing materials because they are more electropositive and more difficult to diffuse than structures with smaller pores.[19]
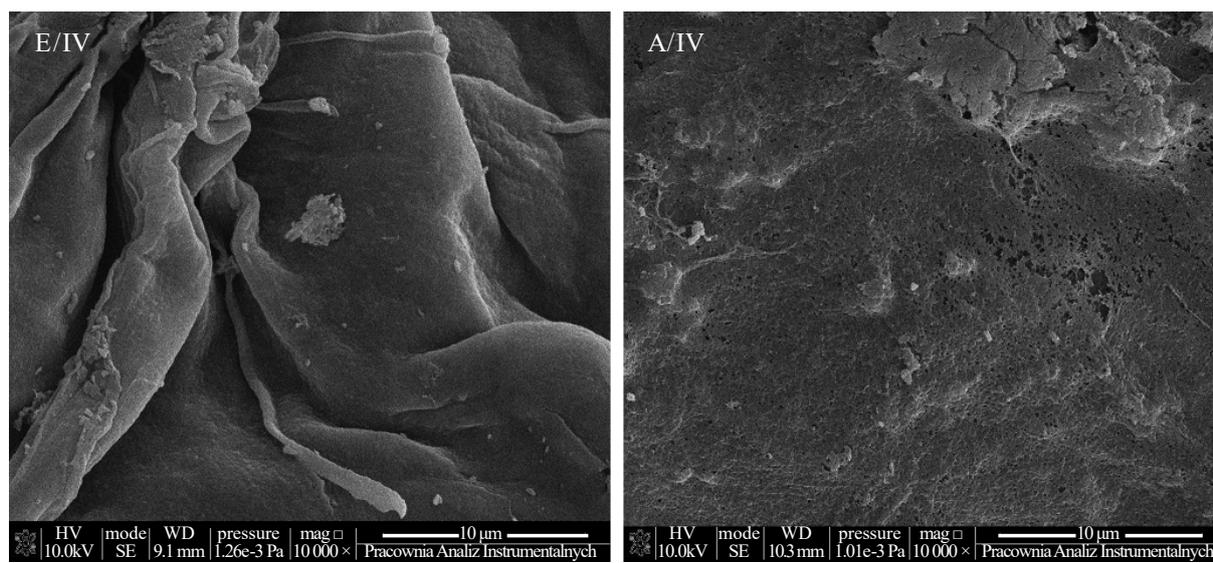

Figure 2. Porosity of sample E (without crosslinking agent) and sample A (containing the smallest amount of crosslinking agent) both dried using dM4 method

4. Conclusions

In the case of hydrogel, superabsorbent polymers post-synthetic drying is crucial for the sorption characteristics of the material. It was shown that the best drying methods include freezing of water contained inside the polymer network and its further sublimation. The porosity largely depends on the size of the ice crystals inside the frozen channels, so it can be concluded that when ice sublimation occurs more rapidly at a lower freeze pressure, the internal structure of the scaffolds is more open. During the drying step, the rate of sublimation can be influenced by two parameters: the ambient temperature and the pressure in the chamber facilitate sublimation by controlling the thermal transfer between the frozen product and the environment.[20] The higher is the pressure applied during drying, the longer is the sublimation process, which leads to the formation of a network of smaller pores. This conclusion is in line with the results of the swelling experiments.

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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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