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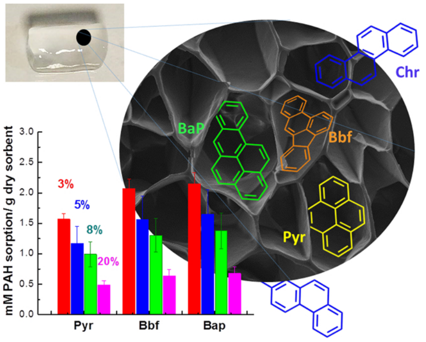
Rheological characterization of starch gels: A biomass based sorbent for removal of polycyclic aromatic hydrocarbons (PAHs)

Deniz Ceylan Tuncaboylu[a,*], Suzan Abdurrahmanoglu[b,*], Isil Gazioglu[a]

[a] Bezmialem Vakif University, Faculty of Pharmacy, 34093 Istanbul, Turkey
[b] Marmara University, Department of Chemistry, 34722 Istanbul, Turkey

GRAPHICAL ABSTRACT



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ABSTRACT

Environmental awareness increased the demand for the biomass based materials with superior properties instead of petroleum products. This study aims to prepare starch networks as sorbents for the removal of polycyclic aromatic hydrocarbons (PAHs). Two types of crosslinker, epichlorohydrine (ECH) and glutaraldehyde (GA), were choosed for the preparation of Gel-E and Gel-G networks, respectively. Rheological, swelling and morphological properties of the resulted materials were investigated as a function of various reaction parameters as starch, crosslinker and base concentration and also reaction temperature. The rheological measurements showed that while network formation of Gel-E hydrogels was strongly affected by the NaOH and starch concentration, the strength of the Gel-G hydrogels mainly depends on the crosslinker amount. Starch networks showed high PAH sorption capacities up to 1.42 g per gram sorbent with three model PAH molecules. Although PAH sorption capacities of the Gel-E networks are higher than those of Gel-G gels due to the pore sizes differences of the gel samples, both of them are promising materials as biosorbent for the PAH sorption applications due to the relatively high sorption capacities, low cost and simple preparation methods.

1. Introduction

Recently, due to increasing environmental awareness and the legislations, biomass-based materials have received much attention as an alternative to the petroleum synthetic polymers for the preparation of hydrogels because of their biocompatibility, biodegradability, non-toxicity, and plenty in nature [1]. Among the carbohydrate family, starch is the second most abundant member in nature which is

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* Corresponding authors.
E-mail addresses: dtuncaboylu@bezmialem.edu.tr (D. Ceylan Tuncaboylu), suzanamarmara@edu.tr (S. Abdurrahmanoglu).

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relatively an inexpensive biopolymer derived from readily available sources [2]. Starch is composed of a mixture of two polymeric carbohydrates: linear amylose and branched amylopectin [3,4]. Depending on their botanical source, molecular weight and degree of polymerization of amylose and amylopectin and their ratio and thus the properties of the starch vary a lot [5]. Typically, corn and potato starches have a 20–30 % (w/w) content of amylose and 70–80 % amylopectin [6]. Chemical modification of starch is being used to introduce desirable properties to starch for specific applications. Crosslinking of starch by reaction with bi- or polyfunctional reagents is widely used in numerous industrial applications such as preparation of wet-rub-resistant starch paper coatings, permanent textile sizes and water-resistant adhesives [2]. Crosslinking reinforces the already present hydrogen bonds in the granules with new covalent bonds. As a result, crosslinked starch is more resistant to acid, heat and shearing than native starch and is thus suitable for applications such as in canned food [3]. Among the other crosslinking agents, epichlorohydrin (ECH) is the most common one used in polysaccharide chemistry [7].

At ambient temperatures, the starch polymers, in the form of granules due to the hydrogen bonding between amylose and amylopectin units, are insoluble in water with a relatively little swelling. However, through the increasing temperature of water, the granules swell and rupture by the destroyed crystalline arrangement as the hydrogen bonds are broken and the granules swell to their maximum as an amorphous suspension. Starch undergoes an irreversible transition: during heating; gelatinization. Polysaccharides can be processed in different ways but their ability to form gels under specific conditions is particularly interesting [8].

Polycyclic aromatic hydrocarbons (PAHs), containing two or more aromatic rings, are in the list of European Union and the U.S. Environmental Protection Agency as priority pollutants due to their teratogenic, carcinogenic and mutagenic activities [9]. PAHs originate from a variety of sources, such as incomplete combustion of coal, petroleum products, wood and organic polymer compounds [10,11]. Due to their chemical stability and low degradability, they ubiquitously accumulate in water sources [12]. Among the others, sorption is the most common used process to remove pollutants in view of high efficiency, low cost, simple operation and easy to find various natural and synthetic sorbents [13,14]. Starch and its derivatives have been widely used as sorbents for the wastewater treatment in environmental technologies [15,16] because of its natural abundance and biodegradability besides many other applications of starch in food industry such as a thickener or a stabilizer etc [17,18]. Starch hydrogels could be an environmentally friendly alternative to synthetic superabsorbents of the polyacrylate or polyacrylamide type, which possess some drawbacks (e.g. low biodegradability, residual contents of carcinogenic monomers, deterioration of the soil structure) [8,19].

In this work, we focused on investigating the influence of crosslinker used for gelation reaction on the properties of starch gels as sorbent. For this purpose, two different crosslinkers which are ECH and glutaraldehyde (GA) were chosen for gelation of starch. In addition, the mechanical behavior of starch gels was also examined by rheological measurements. Although there are many studies about the gelation process of starch, only few of them focused on the rheological characteristics. The experimental results of this study will make valuable contributions to the literature since the properties of starch, particularly rheological behavior vary by its botanical sources. Synthesized hydrogels were used as sorbent to remove various PAH model compounds from their solutions. Although PAHs are individual components, they are always in admixture. Therefore, a mixture of PAH solutions was used to determine sorption capacities of the starch gels by HPLC.

2. Experimental

2.1. Materials

Soluble starch, glutaraldehyde (GA) (50% wt solution in water) and sodium hydroxide were obtained from Sigma-Aldrich. Epichlorohydrin (ECH) was obtained from Fluka. For the HPLC measurements, chromatography grade acetonitrile was used (Gradient grade for liquid chromatography, Merck, Darmstadt). Deionized water was obtained with the Human Power I purification system, Seoul, Republic of Korea. The following individual standards were used for the identification and quantification of PAH's: Pyrene (Pyr), chrysene (Chr), benzo[*b*]fluoranthene (Bbf), benzo[*a*]pyrene (BaP) purchased from Sigma Aldrich Taufkirchen, Germany.

2.2. Hydrogel preparation

Throughout the study starch gels obtained by using ECH and GA crosslinkers refer as Gel-E and Gel-G, respectively. In a typical Gel-E synthesis, 0.8 g starch was distributed/dissolved in 7 mL water at room temperature and stirred for 15 min. After adding 1 mL ECH, the system was continued to stir for one more hour. On the last step, 2 mL of 50 w/v % NaOH solution was added to reaction solution before transferred into the plastic syringes and also between the plates of Rheometer. Reactions were performed at 24 °C and 50 °C and also at −24 °C in a cryostat to obtain cryogel samples. Gel-E hydrogel synthesis is relatively more complicated than Gel-G. In this procedure, starch was distributed/dissolved in liquid water at 50 °C and stirred for 15 min. Then, 2 mL of GA (0.1% w/v) was added into the system and stirred for 10 s to obtain a homogenous mixture with a total volume of 10 mL. The final solution was transferred into the plastic syringes and also between the plates of Rheometer. This reaction was carried out at 50 °C in a thermostat.

2.3. Swelling measurements

Swelling behavior of obtained starch networks was characterized gravimetrically in aqueous solutions over several days at room temperature until the equilibrium was reached. All swelling measurements were performed in triplicate, with uncertainty indicating standard deviation of measurement data. Swelling ratio of hydrogels with respect to after preparation state was determined gravimetrically by the equation given below.

$$Swelling\ \% = \frac{m_s - m_0}{m_0} x100$$

m_s and m_0 are the masses of the hydrogels after preparation state and swollen state, respectively.

2.4. Rheological measurements

Oscillatory measurements were performed between the parallel plates of a controlled shear rate rheometer (Physica MCR 302 Anton Paar, Germany). The upper plate (diameter 25 mm) was set at a distance of 1 mm before the onset of the reactions. During the rheological measurements, a solvent trap was used to minimize the evaporation and the edges of the system working at 50 °C were covered by silicon oil to prevent drying. The time sweep was measured at 24 °C and 50 °C for the Gel-E and Gel-G hydrogels, respectively, at a frequency of $\omega = 1$ Hz and a deformation amplitude of $\gamma_0 = 0.01$ to ensure that the oscillatory deformation is within the linear regime. The strain sweep was measured at a constant frequency of 1 Hz over the strain range of 1–100% to determine the linear viscoelastic region of the samples. The frequency sweep was conducted at 1% strain within the linear viscoelastic region over the angular frequency range of 0.1–100 Hz. The storage modulus (G') and loss modulus (G'') and *tan* δ were used to evaluate the rheological properties of starch samples. Two duplicate runs were done for each measurement to control reproducibility of the system.

2.5. HPLC measurements

2.5.1. Chromatographic conditions

A Shimadzu HPLC system (Kyoto, Japan) was used, which consisted of the following modules: LC-30AD pump, SIL-30AC automatic injector, DGU-20A degasser, CTO-20A column oven, and RF-20A fluorescence detector. The compounds were separated on PAH column (125 × 4 mm, 5 µm, YMC Technologies, Kyoto, Japan), The conditions were: oven temperature of 30 °C; automatic injection of 2 µL; flow rate of 0.8 mL min^{-1}; following gradient mobile phase (A: acetonitrile, B: water): 65% A for 0–0.9 min, 65–75% A for 0.9–7.0 min, 75% A for 7.0–17.0 min, 75–100% A for 17.0–20.0 min, and 100% A for 20.0–24.0 min, returning to the initial conditions. The compounds were detected with the fluorescence detector at excitation and emission wavelengths of 270 and 390 nm (for Pyr and Bbf) and of 290 and 430 nm (for Chr and BaP). The time of analysis was 24.0 min.

2.5.2. Identification and quantification of the PAHs in the gels

The compounds were identified by comparing the retention times with the individual PAHs standards. The peaks were integrated and quantified using the LabSolutions software (Shimadzu, Kyoto, Japan). Each of the gels was placed in glass tubes and acetonitrile was added to the upper level of the gels. The amount of PAH absorbed by the gels was calculated from the areas of the peaks obtained by injecting an acetonitrile sample from each tube into HPLC. The recovery of the PAH's were determined by analyzing duplicates of each 10 µg/mL spiked sample. Respective concentration levels of the samples were used in the methods. The calculated and expected concentrations (C) of the spiked samples were compared to determine the recovery values using the following equation:

$$\text{Recovery }\% = [C_{\text{spiked sample}}/C_{\text{expected}}] \times 100$$

The limit of detection (LoD) and the limit of quantification (LoQ) were calculated according to the following formulas: C_m + 3SD and C_m + 10SD, respectively, where C_m is mean concentration of PAH in the gel of very low PAH concentration and SD is standard deviation.

2.6. Scanning electron microscopy

Starch samples were coated with Au/Pd before examining their morphology under a high-resolution field-emission scanning electron microscope (JEOL SEM-7100-EDX) at an accelerating voltage of 1 kV. Images were obtained at 10, 50, 200, 250 and 500 × magnifications.

3. Results and discussions

In this study, starch hydrogels and cryogels have been prepared with two different crosslinking agent and thus different reaction conditions. As illustrated in Fig. 1, for the synthesis of Gel-E networks, alkaline conditions are necessary to get a starch anion resulted by a protonation process which will exposed to a nucleophilic attack of ECH. In detail, formation of glycidyl ether linkage on a side chain of starch molecule and then an opening of the epoxide ring by linking to another starch chain causes the formation of crosslinked structure [20,21]. Regarding to the Gel-G synthesis, only mixing certain rates of starch and GA at an optimized temperature is enough to obtain the crosslinked structure.

Initially, reaction parameters; starch and NaOH concentration and reaction temperature have been changed to get optimized conditions for the gelation process of Gel-E as detailed in Table S1. Physical appearance, swelling and rheological measurements were used to decide the required feed compositions of the gels that are potential sorbents for the PAH sorption applications. At least 0.3 w/v % starch concentration is necessary for the hydrogels to be stable to the osmotic pressure during the swelling process in water and applicable for the PAH sorption measurements.

Gel-E hydrogels were prepared between the plates of the Rheometer to investigate the viscoelastic or rheological properties of starch samples to examine the effect of the NaOH concentration. The crosslinking reactions of starch and ECH were monitored using oscillatory deformation measurements at a fixed frequency ω (1 Hz) and amplitude γ (0.01) in order to follow the gradual formation of the three-dimensional starch networks. Gelation kinetics were illustrated in Fig. 2A by a plot of the elastic modulus *G'* against the reaction time at various NaOH concentrations at a starch content of 8 w/v % and ECH concentration 1.28 M. *G'* values are an increasing function of time for 4 h between the plates of Rheometer. Although preliminary experiments showed that the most stable gels were obtained at 8 w/v % starch concentrations, rheological measurements were performed at this and lower starch concentrations to observe viscoelastic characteristics of gels.

Calculated loss factor, *tan* δ, values that reveals the ratio of the viscous and the elastic portion of the viscoelastic deformation behavior were shown as a function of the reaction time in Fig. 2B. For practical applications, a liquid is called ideally viscous if *tan* δ is equals to 100, while a solid material is called ideally elastic if *tan* δ is 0.01. In this study, hydrogels prepared at various NaOH concentrations show viscoelastic behavior with *tan* δ values between 0.12 and 0.01. After a reaction time of 4 h, frequency-sweep tests at $\gamma = 0.01$ were carried out over the frequency range 0.1–100 Hz. Fig. 2C shows frequency-dependence of *G'* (filled symbols) and *G"* (viscous modulus, open symbols). All the hydrogels show a solid-like response, i.e., *G'* shows a plateau over the whole frequency range while *G"* remains on a low level about 2 orders of magnitude smaller than *G'*. The linear viscoelastic region of the Gel-E networks was identified during strain sweep tests in Fig. 2D. The results indicated that the strain value of 1% ($\gamma = 0.01$) in which the time sweep and the frequency sweep tests were done, within the linear ranges for all starch samples. Besides, the networks that have a NaOH concentration lower than15% shows a strain hardening behaviour, the most stable samples are prepared with the lowest NaOH concentration which is durable up to 70% of strain value.

Results of rheological measurements in Fig. 2 were collected in Fig. 3 as column graphs. According to the Fig. 3A and B, while *tan* δ values increasing up to 0.12 as a function of NaOH concentration, % strain at break is decreasing from 70 to 6, *G'* values do not change by the feed concentration of NaOH as shown in Fig. 3C. It has been proved that *tan* δ can reflect the crosslink degree of hydrogels [22,23]. The smaller the *tan* δ is the bigger crosslink degree of the network is. At NaOH contents below 15%, *tan* δ becomes to 0.01, so that they are strong gels with negligible viscous properties and stable up to 70% strain. Therefore, 10% of NaOH was decided to use in the rest of the study for Gel-E hydrogels.

After optimizing the base concentration, to observe the effect of the starch content on the gelation kinetics and then the viscoelastic properties, rheological measurements of Gel-E hydrogels prepared at a fixed NaOH (10%) and ECH (1.28 M) concentrations and various starch contents have been performed and the results were collected in Fig. 4. Comparing the hydrogels varying in starch content, an obvious difference in the gel strength could be seen: *G'* increases with increasing content of the starch concentration from 3 to 8% as illustrated in Fig. 4A. Frequency dependence of *G'* and *G"* for Gel-E hydrogels was shown in Fig.4C. While, all the gels show a solid-like response, a frequency related increase was observed which a decreasing function of starch concentration is. *G'* also changes slightly at a ω value of higher than 2 and 10 Hz for the gels prepared with 3 and 5% concentration of starch, respectively. With strain sweep tests as shown in Fig. 4D, the linear viscoelastic region of the Gel-E networks was identified.

Rheological behavior of Gel-G samples was also investigated at various starch and GA concentrations. Gel-G preparation experiments

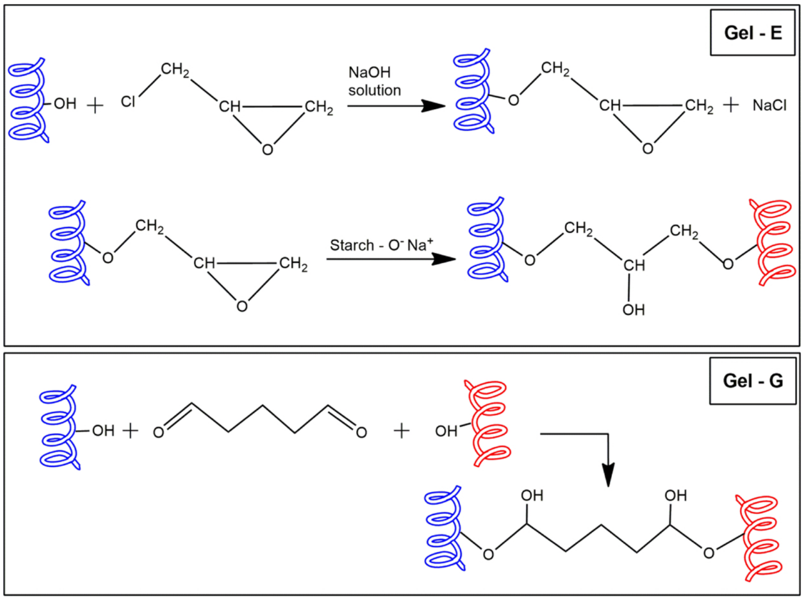

Fig. 1. Crosslinking reactions of starch with ECH (upper panel) and GA (lower panel) to obtain Gel-E and Gel-G network structures, respectively.

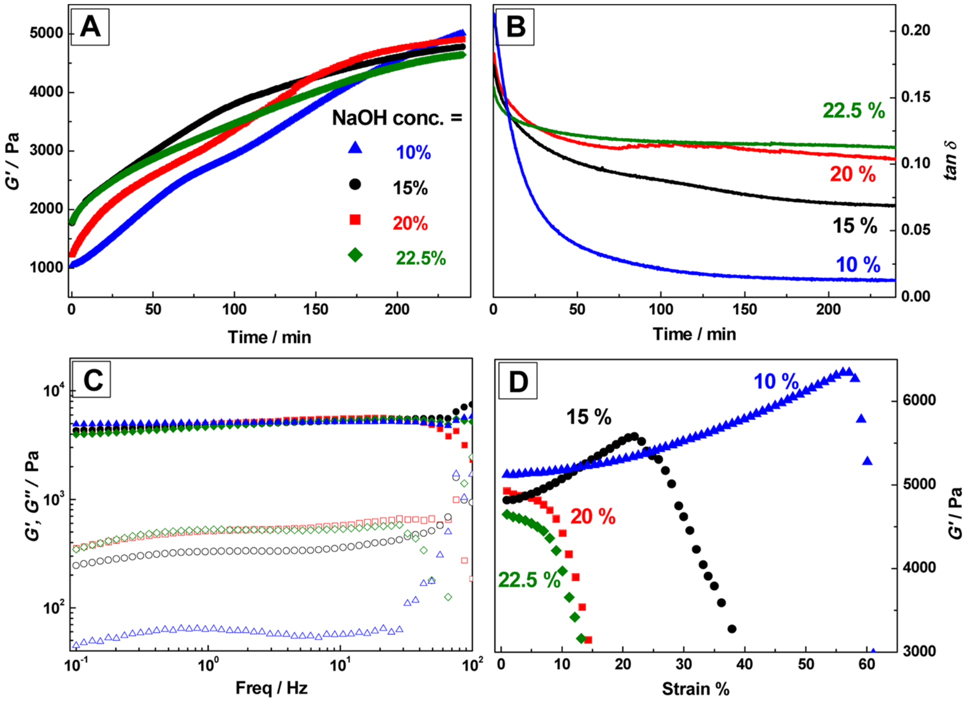

Fig. 2. Rheological measurements of Gel-E hydrogels prepared at 8 w/v % starch and various NaOH concentrations (◆; 22.5%, ■; 20%, ●; 15%, ▲; 10%). **A.** Time sweep, **B.** *tan* δ as a function of time, **C.** frequency sweep, **D.** strain sweep. *G'* (filled symbols) and *G"* (open symbols).

were performed at different gel synthesis temperature (T_{syn}). Results showed that while at the $T_{syn} < 50\,°C$ gel formation was not observed on the other hand when at the $T_{syn} > 50\,°C$ gel solution became heterogeneous due to the high solution viscosity. Therefore, all the gelation reactions for Gel-G were carried out at 50 °C.

The effect of the starch concentration on the mechanical properties of Gel-G structures was examined with two different concentrations as presented in Fig. 5A. Rheological measurements showed that at both starch amount (10% and 20% w/v) hydrogel formation was observed. The comparison of *G'* values implied that increasing amount of starch caused the stronger network formation due to the inter- and intramolecular interactions of sugar chains. The *tan* δ values which are smaller than 1 at both starch amounts also support the strong network structure and formation of solid like behavior (Fig. 5B). According to the frequency sweep test, *G'* and *G"* proceed parallel to each other with an almost constant slope during the whole frequency range for both concentration (Fig. 5C). Besides, *G'* are independent on frequency while *G"* are slightly dependent on frequency above $f = 1$ Hz.

The effect of GA concentration on the gel formation was also examined by rheological measurements. As seen in Figure S1A, at 0.1 w/v % GA concentration, higher *G'* value (22 kPa) is one of the evidence of a strong gel network formation. At a concentration of 0.05 w/v % GA, rather weak network structure was observed. Correspondingly, the *tan* δ value at higher GA concentration is much smaller than that of at lower GA concentrations as shown in Figure S1B.

Fig. 6A shows a plot between relative swelling ratio and swelling time for starch hydrogels and cryogels at room temperature, to study the effect of starch content on swelling. After three days in water, all the gels get their equilibrium state (m_{eq}) independent of the starch concentration and gel preparation temperature. When the starch content

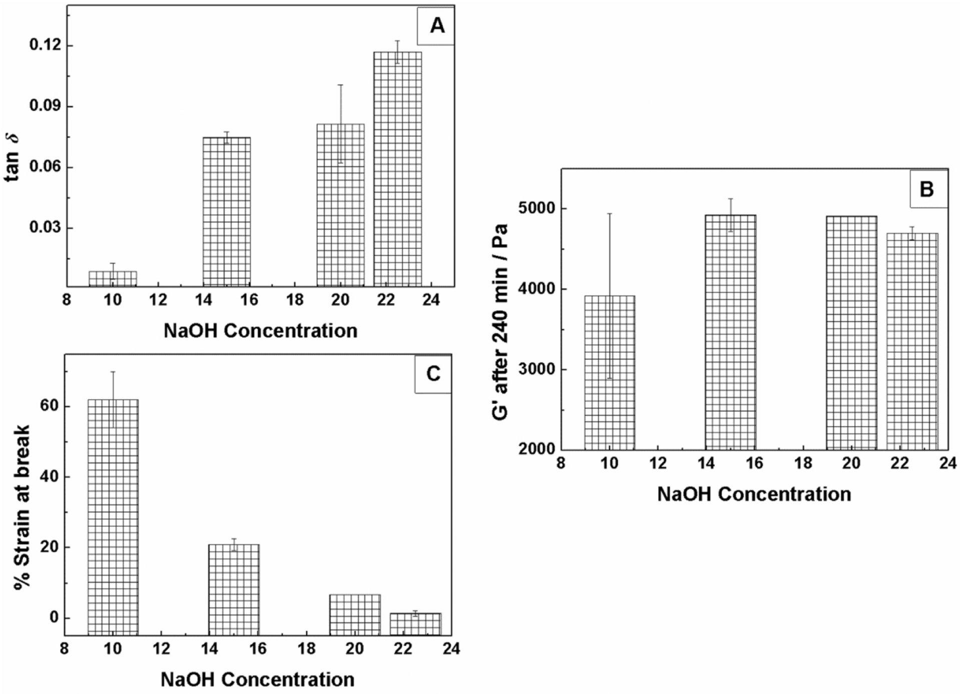

Fig. 3. Column graphical representation of the rheological measurements results of Gel-E hydrogels performed in Fig. 2. **A.** tan δ, **B.** G' after 240 min and **C.** % strain at break values were shown as a function of NaOH concentration.

increases from 3 to 8%, the swelling % of hydrogels decreases gradually from 200 to 50. Similar behavior was observed for the gels prepared at subzero temperature with smaller steps. Swelling kinetics of Gel-G structure is similar with the others where they get an equilibrium state in three days.

Photographs of the equilibrium-swollen states of Gel-E hydrogels (+24 °C) and cryogels (-24 °C) have been taken and collected in Fig. 7 A and B, respectively. While the gels prepared at room temperature are transparent, cryogels are semi-opaque due to the phase separation in the network structure of the gels prepared at freezing temperatures. Diameter of the cryogels is also smaller than the hydrogels.

SEM images of the Gel-E hydrogels have been taken to observe the effect of the starch on the microstructure of the networks (Fig. 8). Independent from the amount of starch, all the gels have a regular, macroporous, interconnected pore structure. While decreasing the starch concentration doesn't change the size of the pores, it has a strong influence on the pore wall thickness which is a decreasing function of decreasing amount of starch.

In the case of cryogels, starch concentration is related to the pore size. As shown in Figure S2, slightly smaller pores have been obtained from left to right with a starch concentration from 8 to 3 w/v%. Such in the Gel-E samples prepared at room temperature, cryogel pore walls

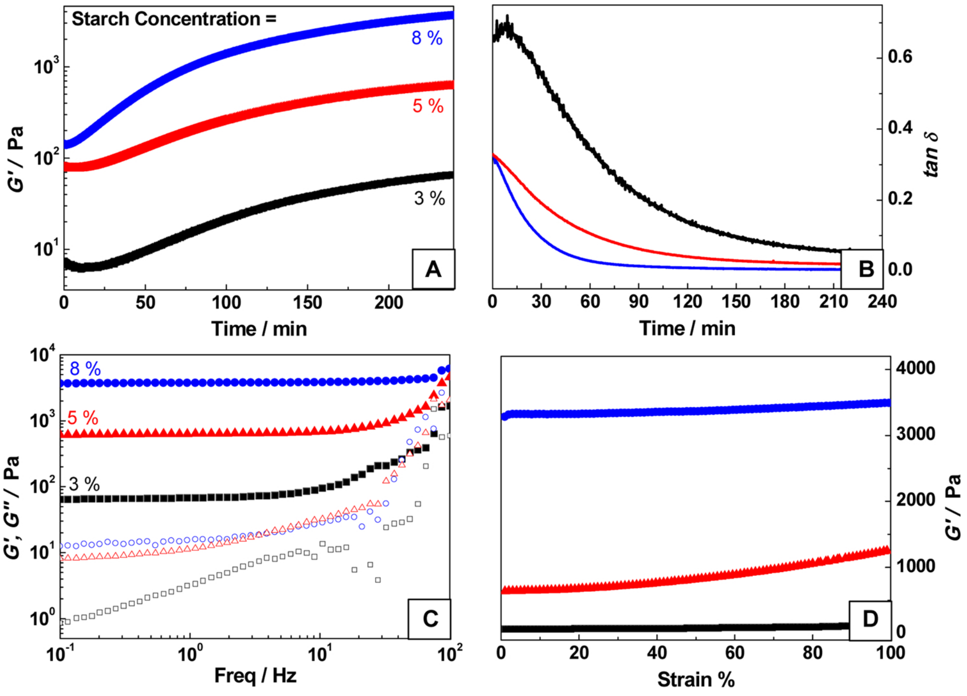

Fig. 4. Rheological measurements of Gel-E hydrogels prepared at a fixed NaOH (10%) and ECH concentration and various starch contents (●; 8%, ▲; 5%,■; 3%,). **A.** Time sweep, **B.** *tan δ* as a function of time, **C.** frequency sweep, **D.** strain sweep. *G'* (filled symbols) and *G"* (open symbols).

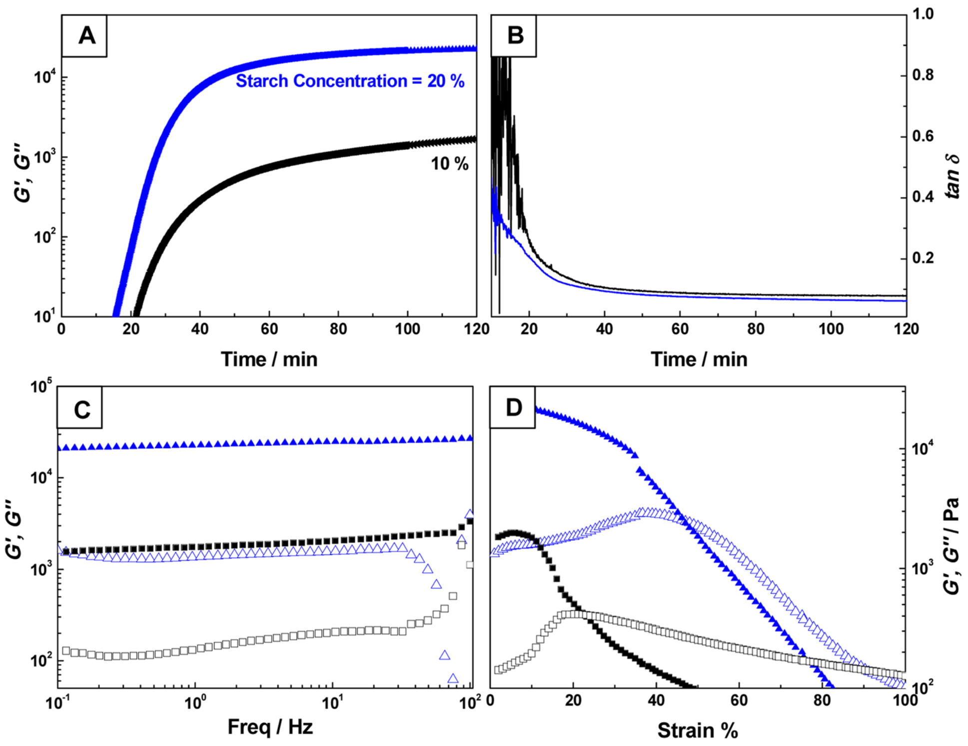

Fig. 5. Rheological measurements of Gel-G hydrogels prepared at 10 and 20 w/v % starch and 0.1% (w/v) GA concentration (▲; 20%, ■; 10%). **A.** Time sweep, **B.** *tan δ* as a function of time, **C.** frequency sweep, **D.** strain sweep. *G'* (filled symbols) and *G"* (open symbols).

thickness are also decreasing with decreasing concentration of starch which is better observed in the lower panel of the images with a magnification of 250 × .

To compare the microstructure of the hydrogels and cryogels, SEM micrographs of Gel-E samples prepared at 3 w/v % have been collected in Figure S3 on left and right panel, respectively. There are two main points that draw attention among the structures. First one is the bigger size of the pores of the hydrogels in comparison with the cryogels. In spite of one generation pore structures in hydrogels, cryogels have additional pores on the pore walls possibly because of the ice crystals during the cryogelation process which is second point observed on the SEM images. Other hydrogels and cryogels which contain 5 and 8 w/v % starch show similar trend on the morphology. But, the differences are much more distinguishable on this concentration

As shown in Fig. 9, Gel-G hydrogels show a macroporous structure. When compared to the Gel-E networks, size of the pores is slightly smaller due to the relatively high amount of starch concentration difference which has a highest value of 8% for Gel-E and 20% for Gel-G hydrogels.

PAH sorption characteristics of synthesized hydrogels and cryogels were determined by HPLC analyses with using a simple method that based on analyzing a mixture of four different PAH molecules instead of an individual sorption of each compound. HPLC standard peaks of the model molecules used for the calculations of sorption capacities of the gels were presented as a function of retention time in Figure S4. Analytical parameters of the HPLC method were also collected in Table S2 that prove the precision of the used method. Initially, kinetic studies were carried out in an incubator adjusted to 24 °C under stirring of 150 rpm. As an example, BaP sorption peaks were shown in Figure S5 as a function of sorption time. All kinetic measurement peaks were integrated and calculated results were collected in Fig. 10 for Pyr, Bbf and BaP. Chr did not indicated in the figure due to the negligible Chr sorption capacities of starch samples to the contrary of its relatively lower molecular weight (M_W). This situation associated with high length-to-breath (L/B) ratio of Chr (1.734) which is defined as the ratio of the longer to shorter side of the PAH molecules with a minimum area among rectangles drawn to enclose the van der Waals radii [24]. Considering the *Mw* of the PAH models, sorption capacity of the Pyr,

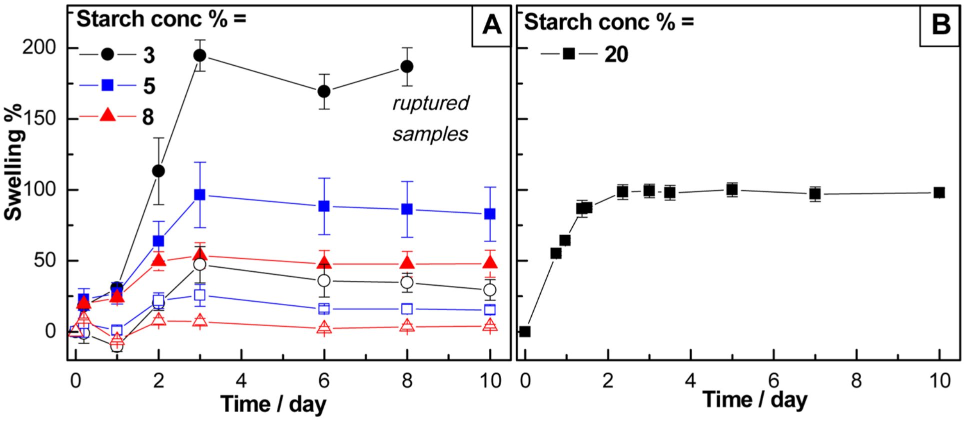

Fig. 6. Water sorption rate of chemically crosslinked Gel-E hydrogels and cryogels with different amounts of starch **A.** Gel-G hydrogels **B.** given as a relative swelling ratio against swelling time.

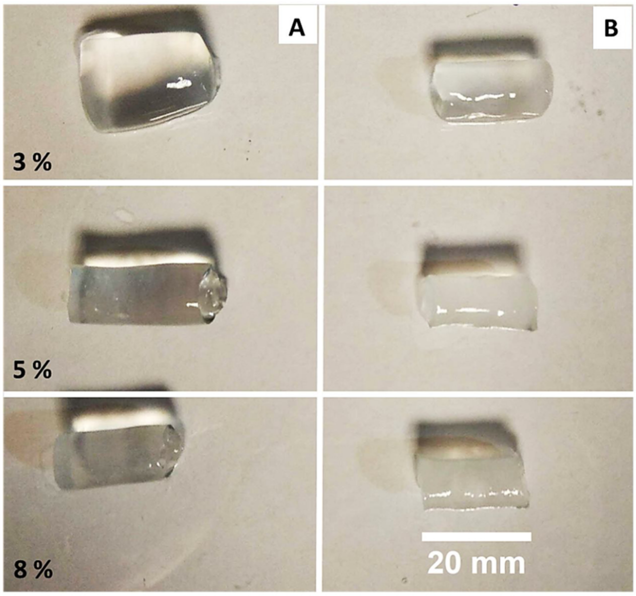

Fig. 7. Digital photos of equilibrium-swollen state Gel-E hydrogels **(A)** and cryogels **(B)** prepared at various starch concentration.

Bbf and BaP molecules similar to each other within the error limits.

Fig. 10B demonstrates the comparison of the Gel-E and Gel-G hydrogel samples. For all the model molecules, sorption capacities of the Gel-E samples are higher because of the higher amount of starch units that leads to the smaller sizes of the pores.

Fig. 11 shows the PAH sorption performances of hydrogels and cryogels after 24 h treatment as a function of starch concentrations, where significant reduction in fluorescence intensity was observed by HPLC spectra. As shown, increasing starch concentration is a decreasing function of PAH sorption capacities of the gels depending on their starch concentration. Another point in the fig. is the slightly higher sorption capacities of the cryogels for the Pyr and Bbf molecules possibly in conjunction with the two generation pore structures in these low temperature gels. In comparison with the reported values of several sorbent materials as butyl rubber sorbent (0.721 mg /g), polyphenol particles (0.75 mg/g) and Poly-CD cryogels (1.25 mg/g), PAH sorption capacities of starch networks are relatively higher [25–27]. Maximum sorption has been obtained for BaP and Bbf molecules as 1.42 and 1.34 mg/g, respectively and a minimum sorption of 0.17 mg/g for Pyr. Besides, the high sorption capacity of the starch samples, their structural integrity was the same at the end of the sorption studies.

4. Conclusion

The synthesis of starch networks was successfully performed in the presence of epychlorohydrine (ECH) and glutaraldehyde (GA) as crosslinkers. Rheological, swelling and morphological analyses were performed to show the effect of the reaction components such as temperature, reactant concentrations etc. on the gelation kinetics and viscoelastic properties of the obtained starch hydrogels and cryogels. Rheological characterization of the Gel-E showed that the base and starch concentrations are highly effective on the strength of network structure of final gels. On the other hand the strength of the Gel-G hydrogels mainly depends on the crosslinker amount. The pollutants that have different L/B ratios were chosen for the sorption experiments in order to show the relationship between the network structure of gels (pore size etc.) and the size of pollutant molecules. Starch networks showed high PAH sorption capacities between 0.17–1.42 mg PAH per gram dry sorbent with three of the selected four model PAH molecules. The results indicated that the sorption capacities of starch based biosorbents prepared in this study are dominated by the pollutants' L/B ratios besides the starch concentrations of gels due to its effect on the pore size. Above all due to the high sorption capacities, low cost and simple preparation methods these hydrogels and cryogels could be suggested as biosorbents.

Acknowledgements

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

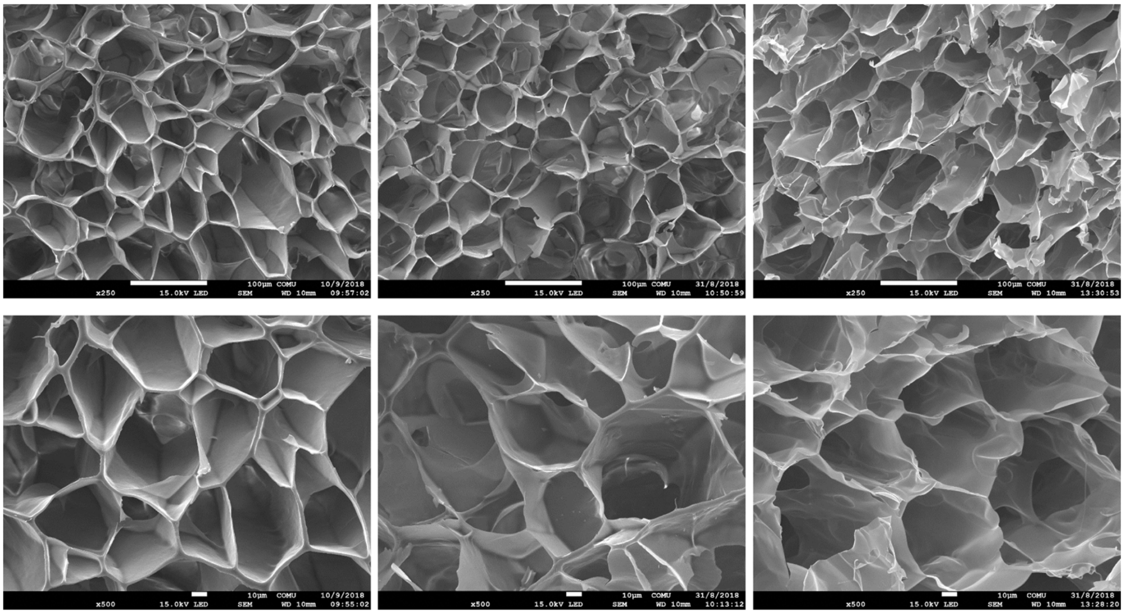

Fig. 8. SEM micrographs of Gel-E hydrogels prepared at +24 °C and various starch concentrations. From left to right: 8, 5 and 3 w/v % starch. Magnifications = 250× (upper panel) and 500× (lower panel).

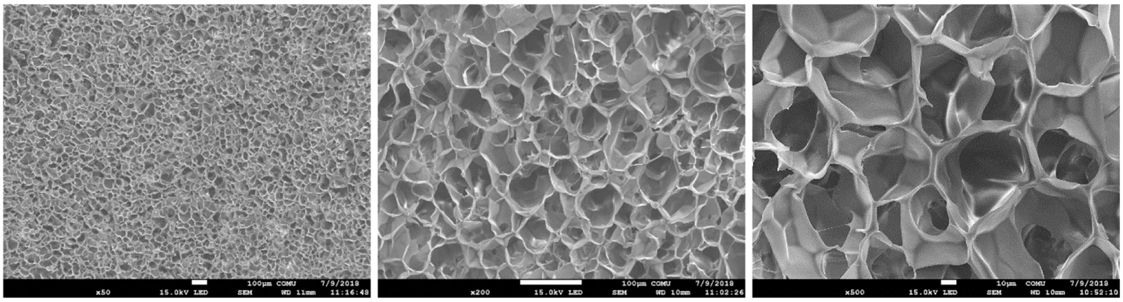

Fig. 9. SEM micrographs of Gel-G hydrogels prepared at 20 w/v starch concentration. Magnifications from up to left to right 50 ×, 200 × and 500 ×.

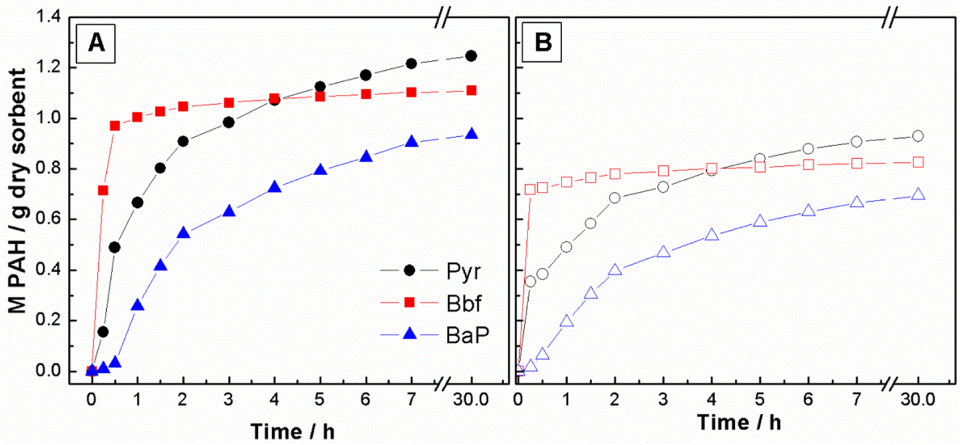

Fig. 10. PAH sorption kinetics of starch gels. **A.** Gel-E hydrogels prepared at 8 w/v % starch. **B.** Gel-G hydrogels. Model PAH molecules: Pyrene (Pyr, circle), benzo[*b*] fluoranthene (Bbf, square) and benzo[*a*]pyrene (BaP, triangle).

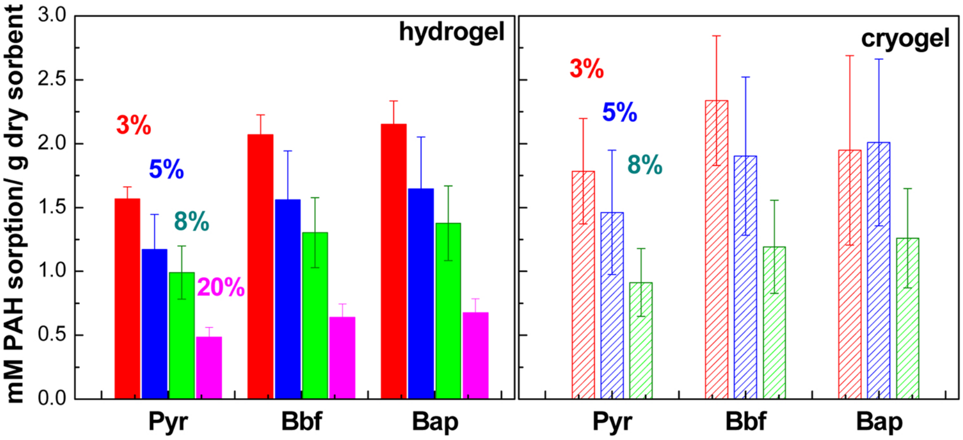

Fig. 11. PAH sorption performance of the starch gels after the 24 h-treatment with solutions of several PAH molecules in acetonitrile. Used starch concentrations are indicated on the Figure. Except 20 w/v % concentration, all bars belongs to the Gel-E networks.

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