30th International Conference Ecological Truth & Environmental Research 2023

Proceedings

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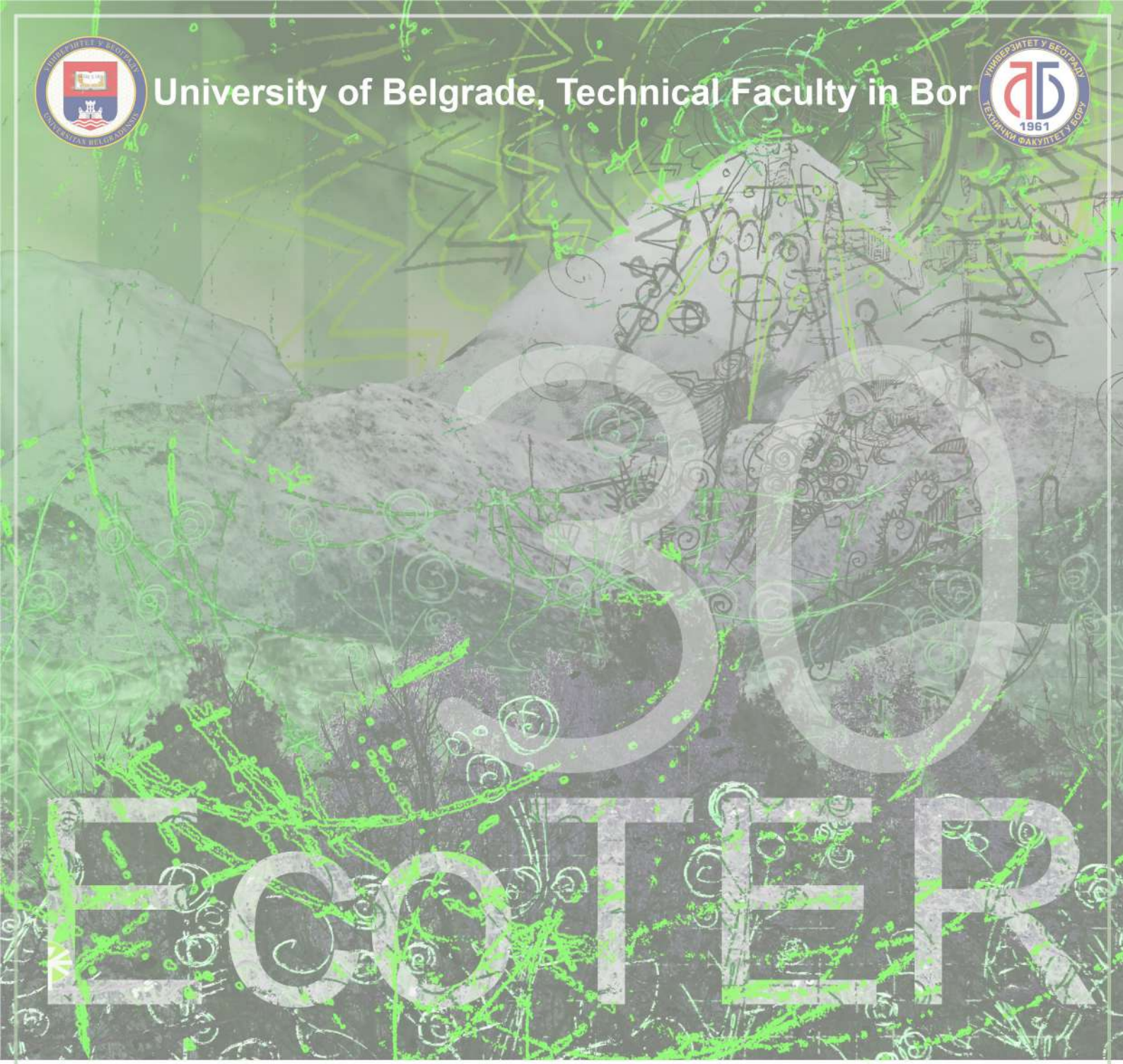

University of Belgrade, Technical Faculty in Bor

30th International Conference Ecological Truth & Environmental Research 2023

Proceedings

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30th INTERNATIONAL CONFERENCE

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PREFACE

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 kept three areas in focus: ecology, environmental protection and sustainable development. The conference will be held on Mt Stara Planina in hotel Stara Planina, Serbia, 20–23 June 2023. The monograph is published on the occasion of the 30th anniversary of the conference. On behalf of the scientific and organizing committee, it is a great honor and pleasure to wish all the participants a warm welcome to the conference.

The monograph is published on the occasion of the 30th anniversary of the conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 30th international conference Ecological Truth & Environmental Research – EcoTER'23 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These Proceedings 103 papers from the authors coming from the universities, research institutes and industries in 11 countries: Australia, USA, Brazil, Spain, Portugal, Libya, Italy, Bulgaria, Bosnia and Herzegovina, North Macedonia, and Serbia.

As a part of this year's conference, the 5th Student Session – EcoTERS'23 is being held. We appreciate the contribution of the students and their mentors who have also participated in the conference.

The support of the Gold donor and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'23. The organizing committee would like to extend their appreciation and gratitude to the Gold donor of the conference for their donation and support.

We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the conference participants for their support to the EcoTER'23. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'23.

Prof. Snežana Šerbula,

President of the scientific and organizing committee

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SUSTAINABLE PECTIN MONOLITH CRYOGELS

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Abstract

The subject of this work is synthesis and characterization of pectin-based cryogels obtained by internal crosslinking with calcium ions. The crosslinking reaction was confirmed by FTIR/ATR analysis, while SEM analysis demonstrated that pores of obtained cryogel were in macro range (between 130 and 380 µm). Pectin cryogel had high swelling degree with the value of 800% after 24 h of immersion in distilled water, and high water vapor permeability (E-7 order, g/ m s Pa). In addition, it showed high rate of biodegradation (85%) after exposure of 3 months in the soil. The obtained results suggest that pectin cryogel obtained by internal crosslinking reaction might find applicable potential in food, agriculture and separation technologies, providing an eco-sustainable approach to tackle current ecological and economical stresses.

Keywords: pectin, cryogels, biodegradation.

INTRODUCTION

Development of sustainable materials have become growing need, due to depletion of fossil fuels and negative impact of petroleum-derived materials on environment and human health. Hence, there is a gained interest to identify new raw materials that are from renewable resources and biodegradable, to convert them into multifunctional materials, and to become an eco-replacement for petroleum-derived materials on market.

Pectin is promising natural biopolymer, that can be utilized to obtain multifunctional biodegradable materials. Namely, it can be found in cell walls of most of the plants. It is mostly extracted from citrus and apple fruits but can be derived from peel waste accumulated in juice industry [1,2]. Pectin has ability to gel in the presence of divalent cations. The mechanism is described as “egg box” model, where divalent cations react with carboxylic groups from pectin, taking chain conformations in shape of egg box [3]. Up to date, pectin is commonly used in food industry due to its nontoxicity and gelling ability, as a stabilizer, compatibilizer or gelling additive [4]. Moreover, due to its 3D network formed in the presence of divalent cations, and biodegradability, it has been widely tested as a biobased matrix for drug delivery, in biomedicine, and for sorption processes [5,6]. However, once when hydrogels are dried under ambient/vacuum conditions, the obtained materials are denser and less porous than starting hydrogel, due to pore collapsing because of high capillary pressure. On the other side, freeze-drying procedure is able to maintain open pore structure of the starting hydrogels. The porosity of final material not only depends on route of drying, but also on crosslinking reaction, and crosslinking density of hydrogels. Regarding the pectin, the

most common crosslinker is $CaCl_2$, where hydrogels are obtained by direct dripping of pectin solution into calcium ion aqueous bath [7]. In contrast, water insoluble calcium-salts can be used as an internal crosslinkers, by dispersing them in pectin solution, and allowing uniform distribution before gelation occurs. The release of calcium ions from $CaCO_3$ is stimulated by d-glucono-δ-lactone (GDL), which hydrolyze slowly within the time, lowering the pH of solution, and allowing better internal crosslinking of calcium ions with pectin chains [8].

Hence, the aim of this work is to internally crosslink the pectin chains in the presence of $CaCO_3$ and GDL and freeze-dry to obtain 3D network with preserved porous structure. The obtained material was subjected to several different characterization techniques, in order to evaluate structural, morphological, water-related and biodegradation properties.

MATERIALS AND METHODS

Chemicals

Amidated pectin, with a degree of methylation of 38%, was obtained from Herbstreith & Fox KG, Pektin-Fabriken (Neuenburg, Germany). $CaCO_3$ and GDL were purchased from Sigma Aldrich (St. Louis, MO, USA).

Preparation of pectin cryogel

Calcium carbonate (200 mg) was finely dispersed in 100 mL of water by sonication (Vibracell VC 505, Sonics, Newtown, USA) for 10 min at 500 Hz (50% of amplitude). 1 g of pectin was dissolved in the aqueous suspension. Afterwards, GDL was slowly added in mixture and set down to allow formation of hydrogel. The ratio GLD/Ca^{2+} was 4:1. The resulting mixture was immediately poured into a petri dish (36 mm diameter) and allowed to set in air for 24 h at room temperature. The obtained polysaccharide hydrogel sample was frozen in round bottomed flasks in liquid nitrogen and freeze dried for at least 24 h on an VirTis SP Scientific Sentry 2.0 freeze drier. The drying conditions were as follows: vacuum set to 100 mTorr and a condenser temperature of -80.0 °C.

Characterization

Fourier-transform infrared spectroscopy (FTIR/ATR)

FTIR analysis was performed by a Perkin Elmer Spectrum 100 spectrometer (Waltham, USA) equipped with a diamond crystal Perkin Elmer Universal ATR sampling accessory. Spectra were recorded on pectin and pectin/alginate films as an average of 16 scans in the range 4000–400 cm^{-1}, with a resolution of 4 cm^{-1}.

Scanning electron microscopy (SEM)

The morphology of the obtained cryogel was scanned on FEI Quanta 200 FEG Scanning Electron Microscope (SEM) (Oregon, USA) at accelerating voltage of 10 kV. Prior to the SEM analysis, the cryogels were sputtered with gold (~7 nm).

Water related properties

The swelling degree (SD) of cryogels was determined by gravimetric method. The cryogels were weighed (m_0, g) and placed in 100 mL of distilled water at room temperature (25 ^oC). The cryogels were taken out from water after 24 h; the excess of water from the

surface was removed by filter paper and the weight of the swollen aerogels (m_{t1}, g) was measured. The swelling degree was calculated by the following equation:

$$SD(\%) = \frac{(m_{t1} - m_0)x100}{m_0} \quad (1)$$

The solubility test was determined as the content of dry matter solubilized after 24 h in distilled water. The swollen cryogels were taken out after 24 h and dried until constant weight (mt_2, g) in an oven at 105 °C. The solubility degree (SLD) was calculated according to following equation:

$$SLD(\%) = \frac{(m_0 - m_{t2})x100}{m_0} \quad (2)$$

The water vapour permeability (WVP) trough cryogels was determined gravimetrically by wet cup method according to the ASTM E96 standard. Cryogels were sealed in a 3 mm circular opening of a glass vial-permeation cell containing water (~100% relative humidity inside the cell). The permeation cell was kept in a chamber with controlled relative humidity of 50% at 25 ^{o}C. The change in weight of the permeation cell was followed in period of 24 h. The WVP of the films were calculated using the following equation:

$$WVP = \frac{\Delta G x l}{t x A x \Delta p} \quad (3)$$

where ΔG was the weight change (g), t was the time during which ΔG occurred (h), A was the test area cup (m^2), l (m) was the thickness of the film and Δp was the water pressure difference between both sides of the cryogel (Pa). Measurements were performed in triplicate and average data were used for calculations.

Biodegradation test

The biodegradation test was performed in soil and the weight change of sample was monitored within 3 months. Prior the test, samples were wrapped in nylon mesh to prevent losing of material during experiment. The humidity and temperature of the experiment were maintained constant. The sampling was performed every 2 weeks, and samples were rinsed with distilled water and dried at 50 °C to constant mass. The percentage of biodegradation rate was calculated according to the following equation:

$$Bio\,deg_{rate} = \frac{(m_0 - m\ )x100}{m_0} \quad (4)$$

where $Biodeg_{rate}$ is biodegradation rate, m_o (g) was initial weight of sample and m (g) final weight of sample after exposure to the soil for the period of 3 months.

RESULTS AND DISCUSSION

FTIR/ATR

The FTIR/ATR spectrum of obtained cryogel is presented in Figure 1. Pectin/$CaCO_3$ cryogel shows a broad, intense area of absorption between 3600 and 3000 cm^{-1} related to -OH stretching vibrational modes, due to inter- and intramolecular hydrogen bonding of the galacturonic acid. The presence of moderately intense bands, in the range of 3000–2800 cm^{-1},

is ascribed to CH, CH_2, and CH_3 stretching and bending vibrations. Strong absorption bands occurring at 1745, 1660 and 1600 cm^{-1}, are attributed to the ester carbonyl (-$COCH_3$) groups, amide groups and asymmetrical stretching band of carboxylate ion (COO-), respectively, whereas the COO- symmetric stretching can be detected at 1415 cm^{-1}. In the range of 1360 and 800 cm^{-1}, moderate absorption peaks, commonly referred to as the "finger print" region related to C-O-C and C-C bonds of carbohydrate ring, can be found. From the analysis of spectrum, it is worthy to underline that the intensity of ester groups is lower than that of carboxylated residues; this outcome confirms the pectin low esterification degree, as previously determined by means of titration method.

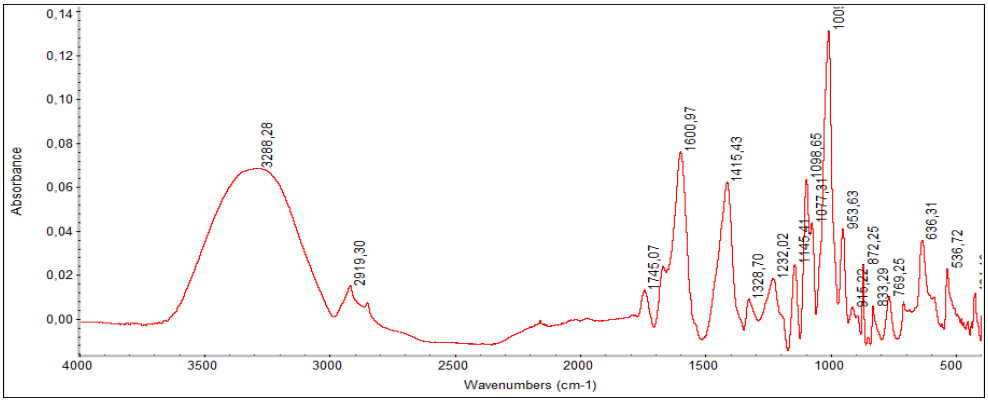

Figure 1 *FTIR/ATR of pectin/$CaCO_3$ cryogel*

SEM

The morphology of pectin/$CaCO_3$ cryogels is displayed in Figure 2. SEM analysis reveals the macroporous system with large number of disconnected voids. The voids diameter ranges between 130 and 380 µm. This result is expected, since this type of structure is common for samples that are freeze-dried for prolonged time, because the longer time of drying promotes growth of crystals. A similar morphology is reported in literature for other pectin cryogels, as well as for starch and alginate cryogels [2,9–11].

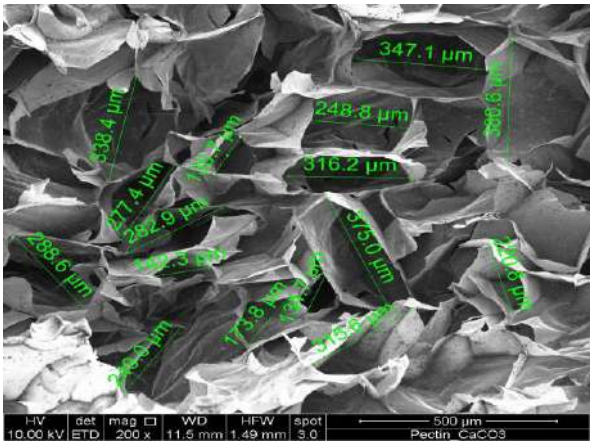

Figure 2 *SEM micrograph of pectin/$CaCO_3$ cryogel*

Water related properties and biodegradation

In order to evaluate the stability of obtained cryogel, solubility, swelling and permeability test in aqueous solutions was performed and results are presented in Table 1. The internal gelation of pectin shows to be efficient, since the solubility of final cryogel is only 5%. On the other side, the obtained cryogel is characterized by high uptake of water, and high water vapor permeability, probably due to voids of large diameters in their structure. Finally, the obtained material demonstrates high level of biodegradation in soil, reaching a value of 85% after 3 months of exposure. There are no published data related to biodegradation rate of pectin cryogels for long exposure time. Chen *et al*. [12] reported 60% of pectin/clay cryogel biodegradation after 1 month of exposure in compost media. On the other side, a biodegradation rate of 63% in a period of 30 days was achieved by the respiratory method for externally crosslinked cryogels [2].

Table 1 *Water related properties*

SD, %	SLD, %	WVP, g/ m s Pa	Biodegradation rate, %
800	5	$1.5 \cdot E^{-7}$	85

CONCLUSION

In this work the pectin was internally crosslinked by calcium ions and additionally freeze-dried in order to obtain porous 3D materials. The FTIR/ATR analysis confirmed the crosslinking reaction between pectin chains and calcium ions. SEM analysis showed macroporous system with uneven size distribution of voids in the range of 130 and 380 μm. The obtained cryogels demonstrated high ability to uptake large amount of water (800%), low solubility in water (5%), high water vapor permeation ($1.5 \cdot E^{-7}$ g/ m s Pa) and high biodegradation rate (85%), implying that these materials might potentially be used in sorption processes (wastewater treatments, or as insertions in food packages for moisture/gas uptake), or for specific release of nutraceuticals and fertilizers in food/agriculture sectors, providing product sustainability.

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