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SINTEZA HIDROGELOVA NA OSNOVI CELULOZE MODIFICIRANE VINILNIM POLIMERIMA S DUŠIKOM

DOKTORSKI RAD

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SYNTHESIS OF HYDROGELS BASED ON CELLULOSE MODIFIED WITH NITROGEN CONTAINING VINYL POLYMERS

DOCTORAL THESIS

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Sažetak

U ovom istraživanju provedena je sinteza hidrogelova na osnovi modificirane celuloze. Modifikacija celuloze provedena je cijepljenjem celuloze s dimetilaminoetil-metakrilatom (DMAEMA)/vinil-pirolidonom (VP)/vinil-kaprolaktamom (VCLA) dok je metilen-*bis*-akrilamidom (MBA) korišten kao umrežavalo.

Modifikacija celuloze provedena je u otopini, a kao otapalo za celulozu korištena je otopina LiCl u dimetilacetamidu (DMAc). Polimerizacija je najprije provedena uz peroksidni inicijator, a pojedini uzorci su dodatno ozračeni ionizirajućim zračenjem. Nakon provedene polimerizacije priprema hidrogelova provedena je metodom inverzije faza s pomoću deionizirane vode. Kako bi se pripremili uzorci s poroznom strukturom sušenje hidrogelova provedeno je metodom zamrzavanja i ekstrakcije. Sastav i svojstva hidrogelova analizirani su infracrvenom spektroskopijom (FTIR), optičkom mikroskopijom, energetsko disperzivnom rendgenskom spektrometrijom, termogravimetrijskom analizom (TGA), diferencijalnom pretražnom kalorimetrijom (DSC), mjerenjem reoloških svojstava. Ukupan udio polimera, udio mikrogela te stupanj bubrenja određeni su gravimetrijski. Karakterizacija morfologije pripravljenih poroznih uzoraka provedena je pretražnom elektronskom mikroskopijom (SEM). Na strukturu i sastav pripravljene modificirane celuloze najznačajnije su utjecali molarni omjer celuloze i vinilnog monomera u reakcijskoj smjesi te vrsta primijenjenog vinilnog monomera. Provedbom polimerizacije vinilnog monomera u otopini celuloze, pri molarnom omjeru celuloze i monomera 1:1, dobivene su bistre otopine. Nasuprot tome, pri omjerima 1:3 i 1:5, zabilježeno je zamućenje smjese, što ukazuje na prisutnost druge faze. Analizom sastava takvih smjesa utvrđena je prisutnost čestica mikrogela sintetskog polimera.Veličina čestica mikrogela kod uzoraka Cel-PDMAEMA bila je do 30 μm, dok su čestice mikrogela kod Cel-PVP i Cel-PVCLA bile manje od 5 μm.

Infracrvenom spektroskopijom utvrđena je prisutnost karakteristične vrpce celuloze kao i sintetskih polimera: PDMAEMA (C=O), PVP (amid I) i PVCLA (amid I). Na temelju intenziteta karakterističnih vrpca za svaku pojedinu komponentu određen je relativni sastav produkata dobivenih modificiranjem celuloze. Relativni sastav modificirane celuloze također je analiziran termogravimetrijskom analizom, a dobiveni rezultati su u skladu s rezultatima dobivenima infracrvenom spektroskopijom.

S porastom koncentracije monomera u reakcijskoj smjesi zabilježen je porast udjela pripadajućeg polimera u nastalom produktu, kod svih ispitivanih sustava. Istovremeno, ionizirajuće zračenje značajno je doprinijelo polimerizaciji DMAEMA, dok kod polimerizacije

VP nije zabilježena značajna promjena. S druge stane, kod Cel-PVCLA ionizirajuće zračenje doprinjelo je topivosti modificirane celuloze u deioniziranoj vodi te samnjenju udjela polimera nakon pretaloživanja.
Stupanj bubrenja hidrogelova određen je gravimetrijski. Za čistu celulozu iznosi 1722 %, dok se za Cel-PDMAEMA hidrogelove, ovisno o sastavu, kreće u rasponu od 721 do 1533 %, a za Cel-PVP hidrogelove između 1392 i 2054 %. Pripremljeni hidrogelovi pokazuju viskoelastična svojstva slična krutim tvarima, pri čemu je modul pohrane veći od modula gubitka u cijelom ispitivanom frekvencijskom području. Hidrogelovi od modificirane celuloze imaju niže vrijednosti modula gubitka u odnosu na hidrogel čiste celuloze, dok se vrijednosti modula pohrane kreću između 7,3 i 30 kPa. Iz hidrogelova čiste celuloze te celuloze modificirane s PDMAEMA i PVP uspješno su pripremljeni uzorci porozne strukture.

Ključne riječi: celuloza, polimerizacija, vinilni monomer, ionizirajuće zračenje, hidrogel, bubrenje

Abstract

In this study, hydrogels based on modified cellulose were synthesized. The cellulose was modified by grafting of cellulose with dimethylaminoethyl methacrylate (DMAEMA)/vinylpyrrolidone (VP)/vinylcaprolactam (VCLA) while methylene-*bis*-acrylamide was used as crosslinker.

The modification of the cellulose was carried out in a solution, and a solution of LiCl in dimethylacetamide (DMAc) was used as a solvent for the cellulose. Polymerization was initiated with a peroxide-based initiator, while selected samples were subsequently exposed to ionizing radiation. Following polymerization, hydrogels were formed through phase inversion in deionized water. To obtain porous structures, the hydrogels were dried using the freeze-extraction method. The composition and properties of the resulting hydrogels were analyzed using Fourier-transform infrared spectroscopy (FTIR), optical microscopy, energy-dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and rheological measurements. Additionally, total polymer content, microgel fraction, and swelling degree were determined through gravimetric analysis. Scanning electron microscopy (SEM) was used to characterize the morphology of the porous samples.

The structure and composition of the modified cellulose were primarily affected by the molar ratio of cellulose to vinyl monomer and the specific type of vinyl monomer used. When polymerization was conducted with a 1:1 cellulose-to-monomer ratio, the resulting mixtures were clear, indicating a homogeneous system. However, at cellulose-to-monomer ratios of 1:3 and 1:5, the mixtures became turbid, suggesting the formation of a second phase. Further analysis revealed that this turbidity was due to the presence of microgel particles composed of the synthetic polymer. In Cel-PDMAEMA samples, these microgel particles reached sizes up to 30 μm, whereas in Cel-PVP and Cel-PVCLA systems, particle sizes remained below 5 μm

Infrared spectroscopy confirmed the presence of characteristic absorption bands corresponding to both cellulose and the synthetic polymers: PDMAEMA (C=O stretching), PVP (amide I), and PVCLA (amide I). The relative content of each component in the modified cellulose samples were estimated based on the intensity of these specific bands. The relative composition of the modified cellulose was additionally assessed using thermogravimetric analysis, and the results aligned with those obtained from infrared spectroscopy. As the monomer concentration in the reaction mixture increased, a higher proportion of the corresponding polymer was observed in the final product across all tested systems. Ionizing radiation notably enhanced the polymerization of DMAEMA, whereas it had little effect on the polymerization of VP.

Conversely, in the case of Cel-PVCLA, ionizing radiation improved the solubility of the modified cellulose in deionized water and led to a reduction in polymer content following reprecipitation.

The swelling degree of the hydrogels was measured gravimetrically. For unmodified cellulose, it was found to be 1722%, while for Cel-PDMAEMA hydrogels, it ranged from 721% to 1533%, depending on their composition. Cel-PVP hydrogels exhibited swelling degrees between 1392% and 2054%. The synthesized hydrogels had solid-like viscoelastic behavior, with the storage modulus consistently exceeding the loss modulus across the entire tested frequency range. Hydrogels based on modified cellulose showed lower loss modulus values compared to those made from pure cellulose, while the storage modulus varied from 7.3 to 30 kPa. Additionally, porous structures were successfully obtained from hydrogels of pure cellulose as well as from cellulose modified with PDMAEMA and PVP.

The degree of swelling of the hydrogels was determined gravimetrically and is in the range of 1722% for cellulose, 721-1533% for Cel-PDMAEMA hydrogels and 1392-2054% for Cel-PVP. The prepared hydrogels show a viscoelastic behavior as solids and their storage modulus is higher than the loss modulus over the whole range of tested frequencies. Hydrogels made from modified cellulose have a lower loss modulus compared to pure cellulose hydrogel, and the storage modulus values of the prepared hydrogels are in the range of 7.3-30 kPa. Samples with a porous structure were successfully prepared from pure cellulose hydrogels and modified cellulose hydrogels.

Key words: cellulose, polymerization, vinyl monomer, ionizing radiation, hydrogel, swelling