

Structural and Thermo-Mechanical Characterization of Calcium and Barium Alginate Films

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ABSTRACT

The present research addresses the investigation of the mechanical and viscoelastic properties of films consisting of sodium alginate cross-linked with divalent Ca^{2+} and Ba^{2+} ions. Fourier-transform infrared and Raman spectroscopy techniques confirmed the development of the Ca- or Ba-alginate structures. Both techniques revealed a shift of the COO^- vibration modes; The Raman mode assigned to the symmetric carboxylate stretching vibration was slightly shifted from approximately 1593 cm^{-1} to 1597 cm^{-1} or 1603 cm^{-1} in the spectra of Ca- and Ba-alginate films, respectively. TMA analyses performed revealed that increasing the Ca and Ba molarity and immersion time resulted in an increase in the glass transition temperature (T_g) and the strain of the Ca- and Ba-alginate films. This rising trend in T_g was attributed to the less mobility of the molecular chains of polymer as well as the enhanced degree of cross linking by prolonging the curing time or increasing the divalent cation concentration.

Keywords: Polymer, Film, Alginate, Thermomechanical

INTRODUCTION

Alginate is a component of brown algae and is located in its intercellular matrix as a gel. The sequential structure and composition of alginate vary considerably not only among different species but also in the different parts of the same algae [1, 2]. Alginate exhibits a backbone of (1.4) linked -D-mannuronic acid (M) and -L-guluronic acid (G) residues of widely varying composition and sequence [3]. This polymer can be regarded as a true block copolymer composed of homopolymeric regions, called respectively M- and G- blocks, interspersed within the regions of an alternating structure. D-Alginate based materials, where 'D' can be Na, Ca, Sr or Ba, can be used as adsorbents and bio-polymeric coatings when synthesized as films, membranes, or stable emulsions [2] [4]. The strong affinity of alginates for alkaline earth metals increases in the order $\text{Mg} \ll \text{Ca} < \text{Sr} < \text{Ba}$ [1, 5], is responsible for the strength and flexibility of a sea weed host [5]. Alginates interact with a variety of metallic species through several mechanisms, including electrostatic and ionic interactions, covalent-like bonding,

coordination, and redox reactions [6, 7]. Specifically, alginate cross-linking with Ca^{+2} and Ba^{+2} ions is conducive to strong and water-insoluble films. Furthermore, alginate-type polymeric structures combine biodegradability, biocompatibility and low cytotoxicity, which enable their application in environmental protection, and biotechnology areas. In particular, alginate-based beads and films can also be used for water cleaning due to their ionic-exchange capability for heavy metal ions [8-11]. The structural and chemical control as well as the corresponding mechanical and thermo-mechanical properties will be conducive to the determination of the optimum working conditions for these alginate-based films. On this basis, the present work addresses the effect of the processing conditions and the type of divalent species, Ca or Ba, on the structural and thermo-mechanical properties of the corresponding alginate films.

EXPERIMENTAL

The cross-linking agents were calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and Barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) of (Fisher Scientific, ACS Reagent Grade). Low-viscosity alginic acid sodium salt ($(\text{C}_6\text{H}_7\text{O}_6\text{Na})_n$, MP Biomedicals) was used to produce the precursor sodium alginate (NaAlg) film. All syntheses were carried out using deionized water ($18.2\text{ M} \cdot \text{cm}$). Calcium alginate (CaAlg) and Barium alginate (BaAlg) films were synthesized by immersion technique where the precursor NaAlg film were contacted with aqueous solutions of Ba (0.025M, 0.050M and 0.075M) and Ca ions (0.1M, 0.15M and 0.2M). The duration of the immersion stage ('curing'), where the precursor NaAlg film is contacted with the divalent ion solution, was controlled in the 0.5-24 hours range.

Crystallinity of CaAlg and BaAlg films was studied in a Siemens D5000 X-ray diffractometer. Renishaw Raman spectroscopy with a laser excitation line of 785 nm and FT-IR Affinity-1 model with a single reflection ATR (Attenuated Total Reflection) accessory equipped with a single-bounce diamond crystal were used to study the chemical microstructure. Thermo-mechanical analyzer (Mettler Toledo TMA-SDTA 841e) under a nitrogen atmosphere was used to evaluate the effect of temperature on the mechanical properties of the films.

RESULTS AND DISCUSSION

X-ray Diffraction Analyses

X-ray diffraction (XRD) patterns of precursor NaAlg and Ca- and Ba-alginate films are shown in Figure 1 and Figure 2. The pattern of sodium alginate showed two broad crystalline peaks at $2\theta = 13.5^\circ$ and $2\theta = 21.3^\circ$ [9] [12, 13].

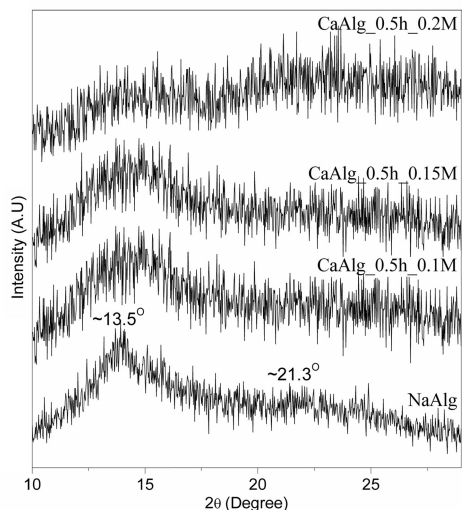


Figure 1. XRD patterns for NaAlg and CaAlg films synthesized with 0.1 M, 0.15 M and 0.2 M of CaCl_2 , and immersion time of 0.5 hours.

NaAlg films exhibit well-defined diffraction peaks, which indicate a better crystallinity and more perfect ordering than the calcium-alginate films [9]. Crystallinity decreases as both, the Ca^{2+} concentration and cross-linking time are increased, which could be due to the incorporation of Ca^{2+} into the matrix of precursor NaAlg film. The broadening in the diffraction peaks of the CaAlg films indicates a very short-range atomic ordering in the polymeric structures. This poor crystallinity makes it difficult to determine the corresponding structure; however, the broad peak at around 13.5° could be interpreted as a lateral packing among molecular chains in the CaAlg structure, whereas the peak near 21.3° may be attributed to the layer spacing along the molecular chain direction [9].

The diffraction patterns of BaAlg films (Figure 2) also exhibited two sharp diffraction peaks at $2\theta = 14^\circ$ and $2\theta = 17^\circ$, suggesting that crosslinking with barium ions promoted the formation of more crystalline Ba-alginate films in comparison to the Ca-bearing ones. It is well-known that barium species binds more strongly to the guluronic acid (G) residues in the alginate chain and the number of residues required for crosslinking to occur is lower compared to calcium ions [14].

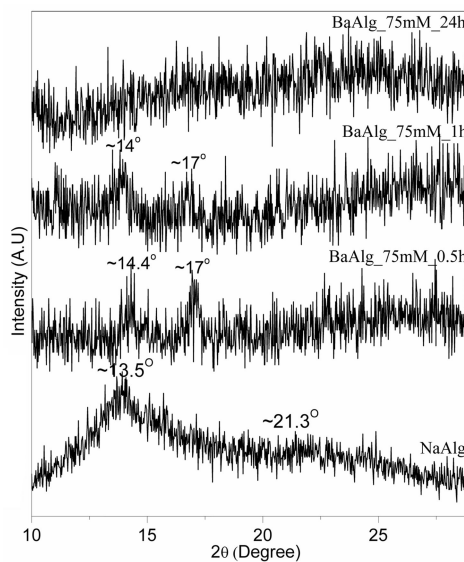


Figure 2. XRD patterns for BaAlg films synthesized after 0.5h, 1h, and 24h of cross-linking time in 75mM BaCl_2 aqueous solution.

Chemical Structure Analyses

Fourier transform infrared spectroscopy, FTIR, can provide direct information of the actual incorporation of the Ca^{2+} and Ba^{2+} ions in the structure of precursor NaAlg films. In Figure 3 shows the FT-IR spectra of NaAlg, CaAlg and BaAlg films. NaAlg displayed two vibrations in the infrared spectrum due to carboxylate group bands (COO⁻). The asymmetrical stretch carbonyl vibration (1597 cm^{-1}) was more sensitive to the presence of the crosslinking agents.

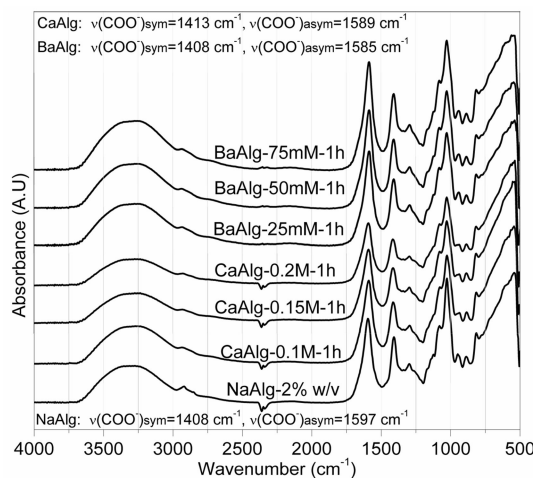


Figure 3. FT-IR spectra of sodium alginate film synthesized by technique immersing in solutions with Ca^{2+} and Ba^{2+} ions for 1 hour.

CaAlg films showed this vibration at 1589 cm^{-1} and the vibration for the BaAlg films occurring at 1585 cm^{-1} . Thus, this band shifts to lower energy as the strength of the ionic interaction between Na^{2+} , Ca^{2+} , and Ba^{2+} species increased inducing a new environment around the carboxyl group [3] [15-17].

Raman spectroscopy analyses evidenced the interaction of the carboxylate group of sodium alginate with the Ca^{2+} and Ba^{2+} ions in the alginate structure confirming its chemical and structural transformation. The modes in the Raman spectra of alginate films can be divided into two groups: vibrations $< 1300\text{ cm}^{-1}$ and stretching vibrations of the carboxylate groups with Raman shifts at 1300 cm^{-1} [18].

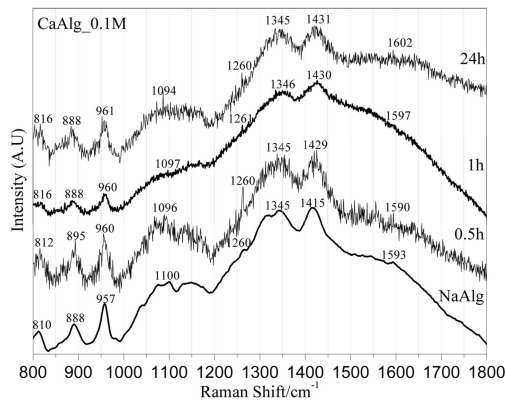


Figure 4. Raman spectra for precursor NaAlg and CaAlg films synthesized at 0.5 h, 1h, and 24 h of immersion time in 0.1 M CaCl_2 aqueous solution.

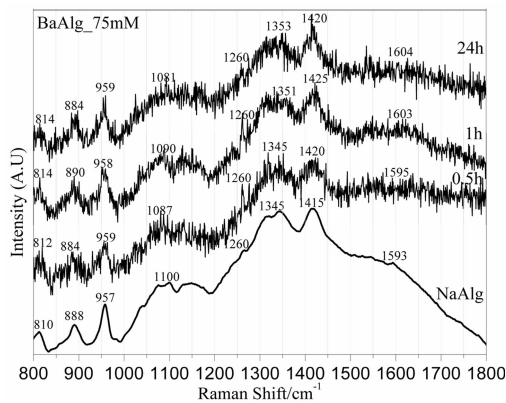


Figure 5. Raman spectra for precursor NaAlg and BaAlg films synthesized at 0.5 h, 1h, and 24 h of immersion time in 75mM BaCl_2 aqueous solution.

The Raman spectrum of Figure 4, and Figure 5, evidence the interactions of alginate with calcium ions lead to changes of band positions as evidenced by the observed shift of the symmetric COO^- stretching band from 1415 cm^{-1} (Na alginate) to 1430 cm^{-1} (Ca alginate) and 1455 cm^{-1} (Ba alginate), respectively. In turn, the Raman mode

assigned to the asymmetric carboxylate stretching vibration was slightly shifted from approximately 1593 cm^{-1} to 1597 cm^{-1} or 1603 cm^{-1} in the spectra of Ca- and Ba-alginate films, respectively. The higher change in the band position ($10\text{--}35\text{ cm}^{-1}$) can be explained in terms of the different G/M unit ratios of polymer expected after the incorporation of different divalent ions in the alginate structure [19, 20].

Thermo-mechanical Analysis (TMA)

TMA analyses of precursor and cross-linked films were carried out using a tensile rig under a load of 0.1N at a $5^\circ\text{C}/\text{min}$ of heating rate. It was found that lower strains were attained in the films produced by contacting precursor NaAlg films with 0.1M and 0.2M Ca and 0.075M Ba solutions for 0.5 and 1 hour of curing, respectively, (Figures 6 and 7). The corresponding glass transition temperature T_g , was estimated at 89.5°C for the precursor NaAlg film under a constant load of 0.1N, whereas it was increased to 91.4°C for the CaAlg film, under the same load (Figure 6-a). This rising trend in T_g was attributed to the less mobility of the molecular chains in the alginate structure as well as the enhanced degree of crosslinking by prolonging the curing time or the concentration of the divalent cation ions.

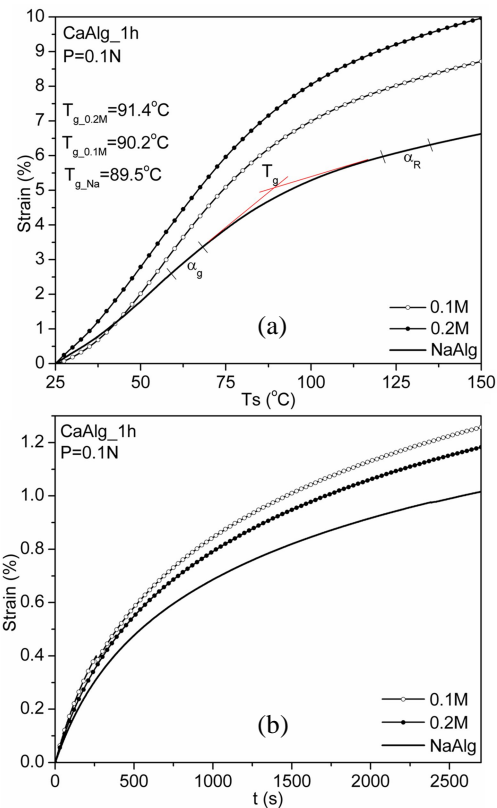


Figure 6. TMA profiles of CaAlg films: (a) heating rate $5^\circ\text{C}/\text{min}$ from 25°C to 150°C ; (b) treated isothermally at 150°C for 45 min. The applied load was 0.1N.

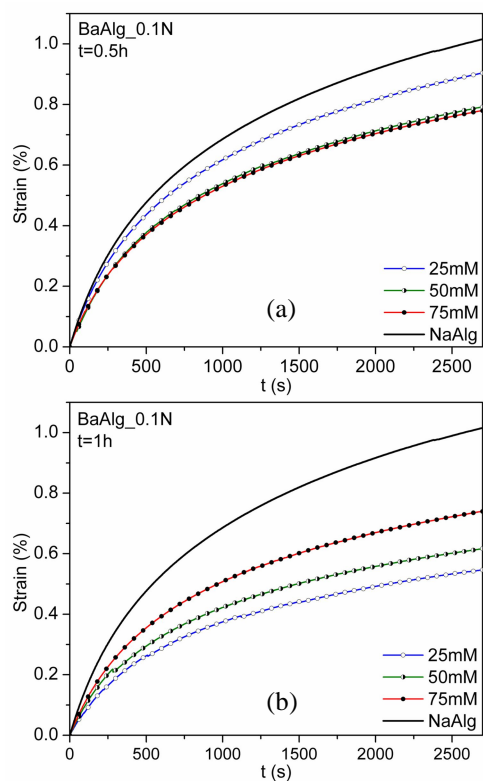


Figure 7. Variation of sample strain as a function of loading time for BaAlg films, treated isothermally at 150 °C for 45 min under 0.1N of load. The curing time was 0.5h, (a), and 1h, (b).

CONCLUDING REMARKS

The formation of calcium alginate from precursor sodium alginate structures was corroborated by XRD, FTIR and Raman spectroscopy analyses. The cross-linking process associated to the formation of calcium alginate was promoted by increasing the Ca and Ba concentration in the reacting solution or by prolonging the immersion time. The increase observed in the glass transition temperature was attributed to the diminution of the mobility of chain segments caused by the actual cross-linking of alginate structures with Ca and Ba ions.

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