Physico–chemical properties of Chitosan films

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Abstract: Chitosan films obtained by dry phase inversion were prepared from an aqueous
solution of chitosan in acetic acid. The films, of thickness less than 20 µm, were transparent,
very flexible and had smooth surfaces. Increasing the film thickness induces an increase of
the internal tensions and the consequent formation of a rough surface. Structural investigations
by X-ray diffraction and Fourier transform IR analysis, showed that the chitosan films, as
prepared, are amorphous. Further annealing to evaporate acetic acid and water traces, changed
the amorphous phase into a more ordered phase, characterized by diffraction peaks at 2θ values
of 9, 17, 20 and 23 degrees. Thermal investigations by TG, DTG, and DTA revealed that the
decomposition of the chitosan films as prepared proceeds in two stages, starting from 180 °C
and 540 °C.

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1 Introduction

Chitosan, (1,4)-[2amino-2-deoxy-β-D-glucan, is a natural derivative of chitin, obtained by
its partial deacetylation. Chitosan is the N-deacetylated derivative of chitin, although this
N-deacetylation is almost never complete. The structure of chitosan is shown in Fig.1.
An agreed nomenclature to describe the degree of N-deacetylation between chitin and chi-
tosan has not been defined [1,2]. Chitosan has an amine side group, which is responsible
for its polycationic character, and for the formation of well-known intermolecular com-

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plexes with carboxylic and polycarboxylic acids [3]. Chitosan is inert, hydrophilic, biocompatible and biodegradable [4-7]. Its biodegradation leads to the release of aminosugars which can be incorporated into the metabolic pathways for glycosaminoglycans and glycoproteins, or excreted [8]. While chitin is insoluble in most solvents, chitosan is readily soluble in acidic solutions and is thus more suitable for industrial applications. Higher molecular weight chitosans have been reported to have good film-forming properties as a result of intra- and intermolecular hydrogen bonding [9]. A number of researches report the preparation of membranes or films, for use in various fields such as in metal-ion separation, gas separation, reverse osmosis, ultrafiltration, evapermeation, pervaporation and for affinity purification [10-13]. The chitosan film characteristics varied in the different studies. Differences in the chitosan material properties, solvents used, method of film preparation, and types and amount of plasticizers used, may affect the quality of the film [14,15].

The objective of this study is to characterize the free standing chitosan films prepared by dry phase inversion from solutions of chitosan in acetic acid.

Fig. 1 Chemical structure of chitosan

2 Experimental

2.1 Materials

Chitosan (M_v = 1,600,000 determined by viscosity analysis of chitosan solutions, and 87.2 % degree of deacetylation determined by infrared spectrometry) was purchased from University of Sherbrooke-Canada, and used without further purification. Acetic acid (Merck, minimum assay 99.0 %) and distilled water were used as solvents for chitosan.

2.2 Films preparation

Chitosan flakes, 0.5 g, were dissolved into 50 mL aqueous acetic acid solution (0.5 wt%) to prepare 4.656×10^-2 eq/L of aqueous acetic acid solution. The mixture was stirred at room temperature for 24 hours, and the solution was degassed by centrifugation at 1500 rpm for 30 min. The resulting solution was clear and yellowish.

The investigated chitosan films were prepared by dry phase inversion, i.e. the solution was poured into Teflon molds and left for evaporation in a thermostat chamber at 50 °C for 24 hours. The thickness of the chitosan films, measured with scanning electron microscope, was within the 20 - 100 μm range. Some films were annealed at 180 °C/30
min under $E = 30 \text{kV/cm}$ electric field, and other films were subject to simple thermal treatment, without an electric field.

2.3 IR spectra

FTIR spectra were recorded on a FT-IR BOMEM MB 104 spectrometer. Spectra were taken with a resolution of 2 cm$^{-1}$ and were averaged over 120 scans, in the range 4000-500 cm$^{-1}$. Powder samples were thoroughly ground with exhaustively dried KBr and discs were prepared by compression under vacuum. The films were investigated by FTIR-ATR technique.

2.4 SEM Study

The morphology of samples was studied by Scanning Electron Microscopy (SEM) on TESLA-BS-300 instrument.

2.5 X-ray diffraction

The structure was investigated with TUR M62 X-ray diffractometer using Cu K$\alpha_1$ radiation, $\lambda = 1.5418$ Å, with Ni filter, $U = 36$ kV, $I = 20$ mA, scanning rate $\omega = 1^\circ$/min.

2.6 Thermogravimetric analysis

Thermogravimetric data were recorded on a Paulik-Paulik-Eddey type Derivatograph MOM, Hungary, which allows simultaneous recording of the weight losses (TG), the derivative (DTG), the differential thermal curves (DTA) and the temperature increases (T), in a static air atmosphere. Aluminum oxide was used as reference material, calcinated at 1000 $^\circ$C. A platinum crucible, heating rate of 8, 10 and 12 $^\circ$C/min, temperature range 10-900 $^\circ$C and a sample weight of 63.3 mg was used.

2.7 TSDC study

The thermally stimulated discharge currents (TSDC) were recorded with a heating/cooling rate 1 K/min, using a computer-controlled Keithley 617 Electrometer and a measurement chamber controlled by a 5700A HP temperature controller.

3 Results and discussion

3.1 FTIR characterization

The FTIR spectrum of chitosan powder shows a broad O-H stretching absorption band between 2800 – 2900 cm$^{-1}$ and the polysaccharide structure between 1155 – 1032 cm$^{-1}$. 
Another major absorption band with 1598 cm$^{-1}$ peak represents the free primary amino group (-NH$_2$) at C$_2$ position of glucosamine. The peaks at 1654 cm$^{-1}$ and 1317 cm$^{-1}$ are amide I and amide II, which indicates that the chitosan used in our investigations is not fully deacetylated.

The most important differences between the FTIR-ATR spectra of chitosan powder, the initially prepared films, and the annealed films are observed in the 1500-1200 cm$^{-1}$ region (Fig. 2), being related to local symmetry changes [16-18]. All the differences in this range are related to the change of the amorphous material into a crystalline phase as indicated by XRD data. The annealed film shows a significant decrease of the 1425 cm$^{-1}$ band, indicating a decrease of CH$_2$ bending ability after crystallization and rearrangement of hydrogen bonds. The vibration mode at 1380 cm$^{-1}$ assigned to CH-bending and C-CH$_3$ deformation appears much less intensely in the annealed film. All bands in the annealed film are shifted to higher frequencies indicating an increase of order in the structure.

![Fig. 2 FTIR spectra of chitosan: (●) powder, (△) as-prepared film and (○) annealed film.](image)

3.2 SEM Study

Figure 3 shows the air-facing surfaces of two chitosan films with different thickness. It is known that a longer drying time at 50 °C, determines the formation of a thinner film with a higher density. Thin films, with thicknesses less than 20 µm, are transparent, very flexible and with smooth surface. Thicker films are quite rigid, brittle, and with scaly surface. The change of the surface morphology suggests that the internal tensions increase with the film thickness.
3.3 X-ray diffraction study

The X-ray diffractogram of an initially prepared chitosan film shows an almost amorphous structure, as reported in other studies of chitosan-acetate films [19]. With thermal treatment in an electric field, $E = 20kV/cm$, a crystalline structure developed, characterized by an important peak at $2\theta = 9$ degrees, and a group of peaks at 17, 20 and 23 degrees. The thermal treatment with no electric field applied to the film, leads to a significantly lower proportion of crystalline material, showing that the electric field plays an important role in the crystallization process (Fig. 4). This result is in agreement with the FTIR-ATR data, where the shifting of all bands to higher frequencies indicated an increasing local order in the annealed films.
3.4 Thermogravimetric study

The thermograms at 10 °C/min heating rate are presented in Figure 5. These thermograms revealed the complexity of the thermal degradation process of the chitosan films as initially prepared.

![Fig. 5 TG, DTG and DTA curves for as-prepared chitosan films.](image)

The thermal characteristics include: the initial temperatures \(T_i\), at which each stage begins, the final temperature \(T_f\) for the end of each phase, the weight loss (W%) corresponding to each interval and DTA characteristics for a heating rate of 10 °C/min are listed in Table 1.

| Stage of thermal degradation | \(T_i\) (°C) | \(T_f\) (°C) | DTA Characteristic | The weight loss (W%) |
|-----------------------------|-------------|-------------|-------------------|---------------------|
| I                           | 180         | 300         | Exo               | 22.53               |
| Stability stage             | 300         | 540         | -                 | 9.28                |
| II                          | 540         | 810         | Exo               | 18.56               |
| Residue                     | -           | -           | -                 | 49.63               |

*Table 1* Thermogravimetric data for initially prepared chitosan films.

From Figure 5 and Table 1, one can observe that the thermal degradation of chitosan films take place in two stages. As expressed in the DTA curve (Fig. 5), the endothermal effect shows that until 180 °C only evaporation of the solvent traces (acetic acid and water), used for chitosan films preparation occurs. Between the first and second stages we found a domain of stability from 300 °C up to 540 °C. Although the TG data reveals a very small slope, no peak could be identified in the DTG data that would suggest a degradation stage. Probably, at the end of the first stage the degradation product becomes stable. The first decomposition stage of the membranes starts above 180 °C and extends to about 300 °C, with maximum decomposition rate around 255 °C. In this stage was observed the most important mass loss, \(W=22.53\%\). It is attributed to a complex process including dehydration of saccharide rings, depolymerisation and decomposition.
of the acetylated and deacetylated units of the polymers [20,21]. The last decomposition stage starts above 540 °C and is probably a thermo-oxidative process [22].

Taking into account the importance of isoconversion methods in thermal analysis [23-25], we have performed kinetic calculations using the method proposed by Vyazovkin and co-workers [26,27]. Their method offers kinetic information regarding activation energy and the pre-exponential factor at different degrees of transformation as well as a formal model for the process. Vyazovkin’s software uses the isoconversion method for calculating Arrhenius parameters, and also the dependence of activation energy on degree of transformation.

Kinetic calculations were performed using the isoconversion method for the first and second stages, in which there are effective processes of thermal degradation in initially prepared chitosan films. The dependences of the activation energy, $E_a$, and the logarithm of pre-exponential factor, $\log A$, on the fraction of reaction, $\alpha$, are plotted in Figs. 6 and 7.

The degree of transformation, $\alpha$, is given by:

$$\alpha = \frac{m_i}{m_t},$$  \hspace{1cm} (1)

where $m_t$ is total mass of the film and $m_i$ is the mass at the $T_i$ temperature.

The models for the decomposition process in the first and second stages are based on the second order kinetics, described by the decomposition function $f(\alpha)$:

$$f(\alpha) = (1 - \alpha)^{-1} - 1.$$  \hspace{1cm} (2)

The calculated activation energy varies with the degree of conversion, indicating that the kinetics of thermal degradation in the first and second stages is complex [27].

![Fig. 6](image)

**Fig. 6** The apparent activation energy as a function of the reacted fraction for the first stage.

### 3.5 TSDC study

The TSDC investigations of chitosan films were performed using load electrodes, in order to leave the films available for other type of investigations. The current records demonstrated the existence of two peaks: a first peak around 50 °C corresponding to a $\delta$ transition due evaporation of acetic acid traces, and a second one around 120 °C.
due to water evaporation. These two current peaks confirm the events seen on the DTG curve. The TSDC current presented in Fig. 8 supports the idea that the amorphous phase crystallizes into a more ordered state after heat and electric field treatment.

For temperatures higher than 200 °C, the current increases rapidly, due to thermal degradation of chitosan.

4 Conclusions

Free standing chitosan films were prepared by dry phase inversion using an aqueous solution of chitosan in acetic acid.

The films of chitosan were transparent with very good flexibility, while thicker films were fragile, showing an increase of internal tension with thickness.

Structural analysis by XRD proved that the films as initially prepared are almost
amorphous. Subsequent annealing converted the amorphous films into a mixture of amorphous and crystalline phases. The crystalline phase is characterized by peaks at $2\theta = 9$, 17, 20 and 23 degrees. The application of an electric field during thermal annealing greatly increased the crystalline volume fraction.

The investigations by TG, DTG and DTA showed that the thermal degradation of chitosan films as initially prepared proceeds in two stages. The first decomposition stage corresponds to a complex series of processes including dehydration of saccharide rings, depolymerisation and decomposition of the acetylated and deacetylated units of the polymers.

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