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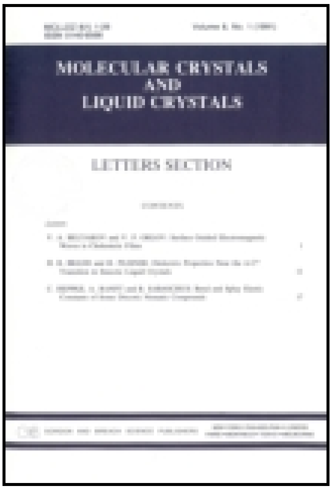

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Thermal Properties of N-Ferrocenemethylchitosan Obtained by Microwave Assisted Method

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Thermal Properties of N-Ferrocenemethylchitosan Obtained by Microwave Assisted Method

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The reaction of ferrocenylmethanol with amino groups of chitosan was carried out in acidic media. FTIR spectroscopy showed that the ferrocenyls exist in the chitosan biopolymer. Thermal stability of N-ferrocenemethylchitosan is different than thermal stability of chitosan. Thermal decomposition of chitosan occurred in two stages, whereas for N-ferrocenemethylchitosan it occurred in five stages. The release of water bonded to chitosan and N-ferrocenemethylchitosan occurred in different way. The structure and properties of modified chitosan are discussed.

Keywords Chitosan; N-ferrocenemethylchitosan; thermal stability

Introduction

Metals containing polymers and biopolymers have emerged as an important category of polymeric materials. Today, ferrocene is being incorporated into polymers to introduce new properties to biopolymeric materials. Examples of these properties include: thermal stability, magnetic behavior, electrical conductivity and possibly superconductivity [1]. The potential use of ferrocene-containing polymers as specialty materials such as those offering unusual electronic, optical and magnetic properties, is still attractive to both academic and industrial interest.

Recently an excellent review on bioconjugates of ferrocene with amino acids, peptides, proteins, DNA, RNA, PNA, carbohydrates, hormones and others was published [2]. High –efficiency dye-sensitized solar cells with ferrocene-based electrolytes has been reported [3].

Chitosan as an important natural polymer is widely studied for a variety of biomedical applications due to its good biocompatibility and biodegradability. Chitosan is characterized by the degree of deacetylation (DD), which allows it to be soluble in dilute acetic acid when DD is $>40\%$. Modified chitosan with ferrocene has been used as a functionalized matrix in electrochemical biosensors to immobilize various enzymes and active agents [4,5,6].

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Ferrocenylmethanol undergoes nucleophilic displacement of the hydroxyl group by amino group of chitosan. The reactivity of the amino groups in chitosan is considerably higher than that of the hydroxyl groups.

The aim of this work was to obtain N-ferrocenemethylchitosan from chitosan by microwave assisted techniques using ferrocenylmethanol. Microwave technology has been used in inorganic chemistry, since the end of 20th century. However, the development of this technique for organic chemistry has been rather slow in comparison to other methods (for example combinatorial chemistry). In microwave technique, the microwave energy is introduced into the chemical reactor remotely. In such a way a direct access by the energy source to the reaction vessel is obtained. The microwave energy passes through the walls of the vessel and it heats only the reactants and solvent. The temperature should increase uniformly throughout the sample leading to less by-products and/or decomposition products. In this work the reaction of ferrocenylmethanol with chitosan was carried out in dilute aqueous acetic acid in a microwave oven.

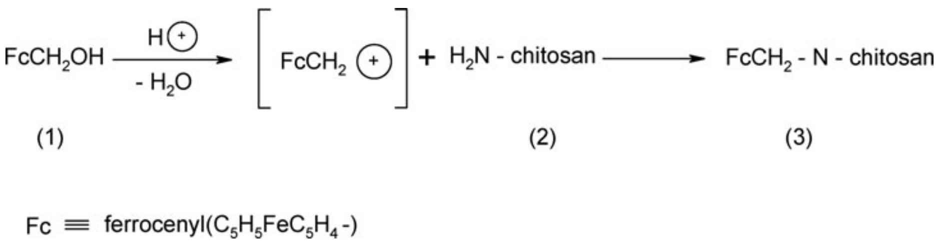
Several methods have been employed to study the properties of obtained material. In this paper the FTIR results as well as TG and DTG results are shown. The structure and thermal properties of modified chitosan are discussed.

Materials and Methods

Chitosan (CTS) of low molecular weight was supplied by Sigma–Aldrich company (Poznan, Poland). The deacetylation degree (DD, %) of chitosan was 80% and it was determinated by the conductometric titration method, taking the first derivative of the conductivity of the chitosan solution (dissolved in 0.1 M HCl) with respect to the volume of the titration solution (0.1 M NaOH) [7]. The molecular weight of chitosan was determined by the viscometric method using the well-known Mark-Houwink equation. The intrinsic viscosity of CTS was measured with an Ubbelohde viscometer in 2% acetic acid/0.2M sodium acetate solution.

The reaction of ferrocenylmethanol with chitosan was carried out in dilute aqueous acetic acid in a microwave oven at 850 W for 12 × 1 min. intervals, waiting 60 seconds between irradiations.

In such condition ferrocenylmethanol reacts with amino groups of chitosan to produce ferrocene bound N-ferrocenemethylchitosan (Scheme 1).



Scheme 1. The reaction of ferrocenylmethanol (1) with amino groups of chitosan (2) to afford the appropriately substituted N-ferrocenylmethyl chitosan (3) in acidic media.

The structure of chitosan and its derivative was evaluated by infrared spectroscopy using a Genesis II FTIR spectrophotometer (Mattson, USA) equipped with an ATR device (MIRacle^{TM} PIKE Technologies) with zinc selenide (ZnSe) crystal. All spectra were

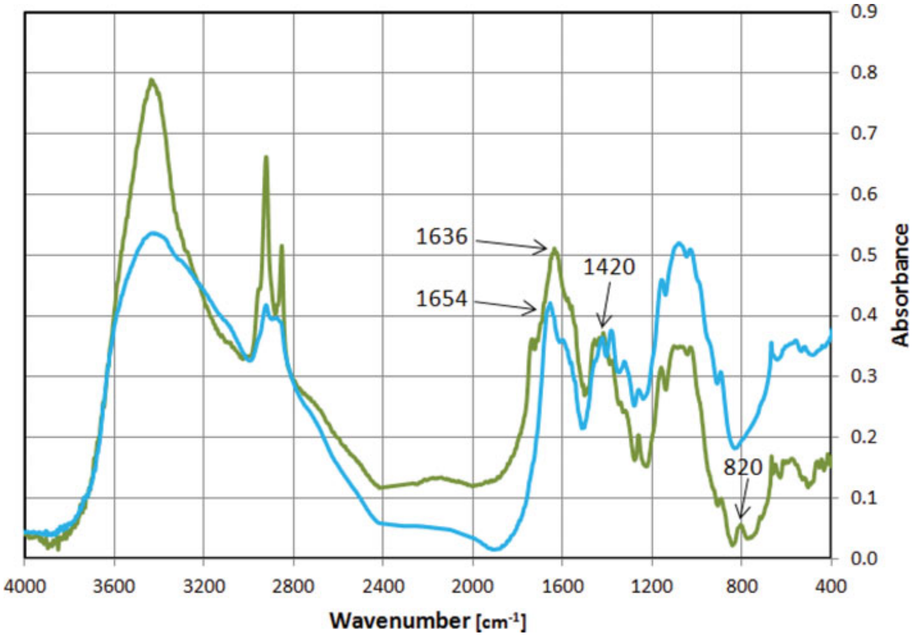


Figure 1. FTIR specta of chitosan (blue line) and chitosan-Fc (green line)

recorded in absorption mode at 4 cm^{-1} intervals and 64 scans. The measurements on all of the samples were repeated at different locations.

The thermal stability of chitosan and its derivative was assessed with *DSC Q200 v24.2 build 107* (TA Instruments, USA). The measurements were carried out with a heating rate of 10°C min^{-1} and a temperature range from 10 to 250°C under a nitrogen flow. The sample mass was in the range ~2–4 mg. Chitosan samples were sealed in an aluminum pan with an empty aluminum pan as the reference.

Thermogravimetric analysis (TG) was performed on a TA Instruments SDT 2960 Simultaneous TGA-DTA in nitrogen and at heating rate 10°C/min and heating programme 25–600°C.

Results and Discussion

The reaction of ferrocenylmethanol with chitosan leads to ferrocene bound N-ferrocenemethylchitosan (chitosan-Fc) (Scheme 1). FTIR spectroscopy showed that the ferrocenyls exist in the chitosan biopolymer. FTIR spectra of chitosan and chitosan after the reaction with ferrocenylmethanol one can see below in Fig. 1. In chitosan spectra one can see characteristic peaks at around 1654 and 1596 cm^{-1}, which are assigned to the amide bands of chitosan [8]. The above amide bands were also observed for chitosan-ferrocene (Chitosan-Fc) derivative, but around 1636 and 1550 cm^{-1}. Due to the N-alkylation of the glucosamine unit with Chitosan-Fc, the intensity of the peak at 1550 cm^{-1}, for primary amine N-H bending, was decreased. Moreover, additional, new absorption bands at 805 cm^{-1} and 1420 cm^{-1}, respectively, in the FTIR spectra also indicate that the ferrocenyls exist in the chitosan-Fc biopolymer. For the ferrocene group usually peaks at 1419, 1096, 1027 and 805 cm^{-1} have been observed [9,10].

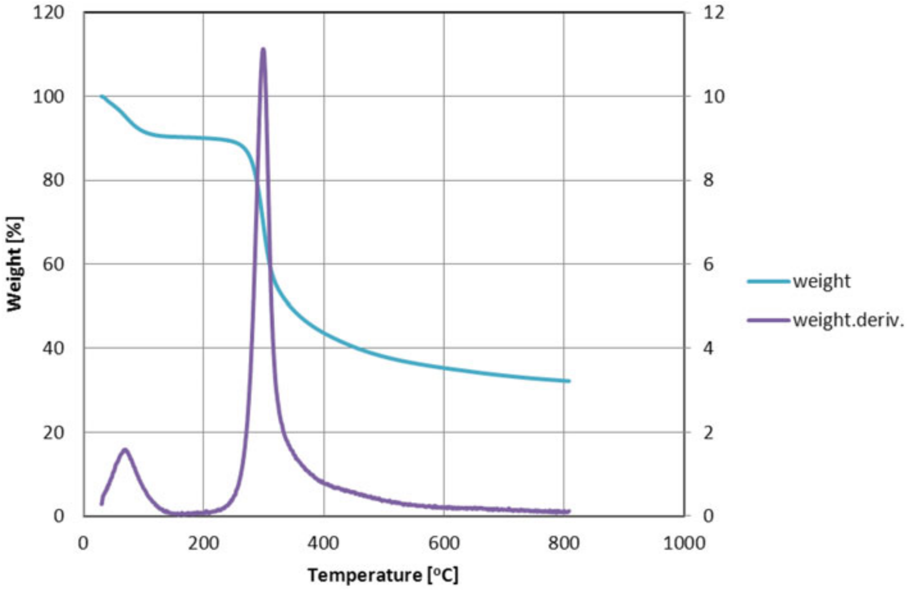


Figure 2. TG and DTG curves for chitosan.

Figures 2 and 3 show thermogravimetric plot (TG) and differential TG (DTG) plots of chitosan and its derivative with ferrocenylmethanol. From TG curves we determined the mass decrement during the heating process. The temperature of the maximum speed of the process (T_{max}) was determined from the maximum on the DTG curve. The comparison of TG plots for chitosan and its derivative with ferrocenylmethanol has been made and it is presented in Fig. 4.

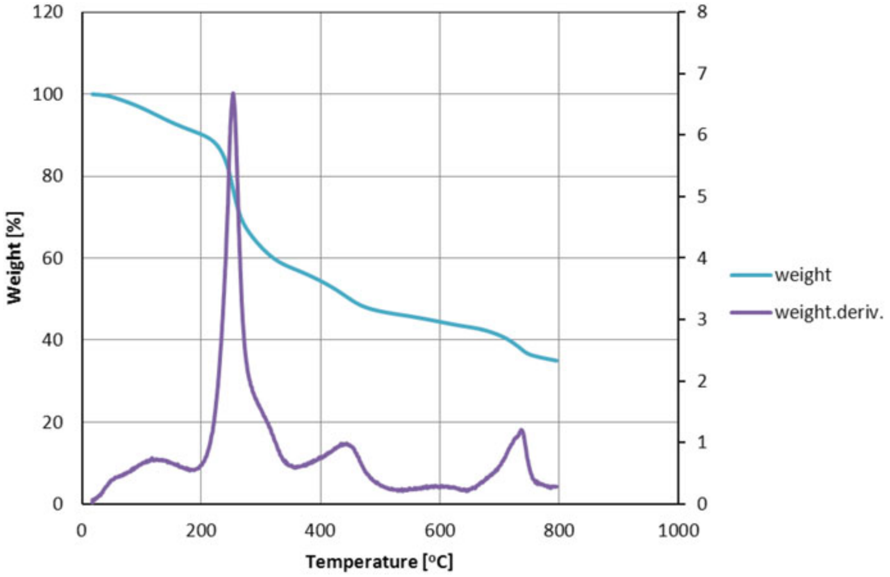


Figure 3. TG and DTG curves for chitosan-Fc.

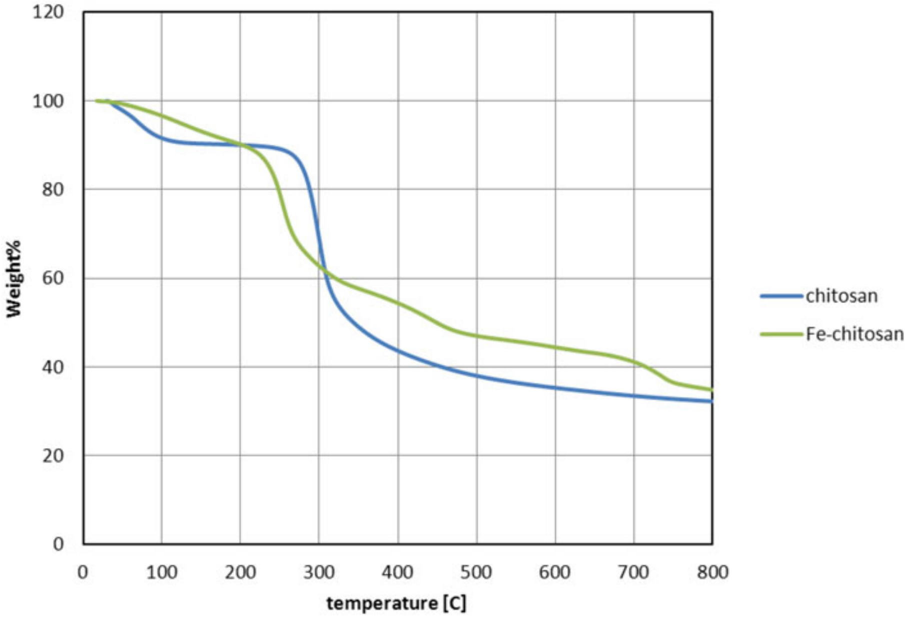


Figure 4. The comparison of TG curves of chitosan and chitosan-Fc.

In Table 1 and Table 2 thermal parameters for chitosan and chitosan-Fc have been presented. In the characteristic DTG curve for chitosan in nitrogen one can see two peaks. These peaks are representative for the two-stage sample destruction due to the temperature.The first stage (between 25 and 150°C) is connected with the evaporation of water absorbed to chitosan. In the second stage (between 250 and 500°C) water bound to chitosan is released and small molecular products of thermal degradation of chitosan are released. In the characteristic DTG curve for chitosan-Fc in nitrogen one can see five peaks (Fig. 4, Table 2). One can conclude that thermal degradation of chitosan-Fc occurs with more stages than that of chitosan.

For chitosan-Fc one can observe that the T_{max} of first stage is much bigger than that of chitosan. However, T_{max} of the second stage is much bigger for chitosan than that for chitosan-Fc. The loss of water absorbed to biopolymer and the weight loss for first stage is bigger for chitosan than for chitosan-Fc. However, the weight loss in the second stage is much smaller for chitosan-Fc than for chitosan. It may suggest that new bonds in chitosan-Fc do not allow water absorption and hydrogen bonding to chitosan chains.

Table 1. The maximum speed of the process (T_{max}) and the mass decrement during the heating process of chitosan determined from TG and DTG curves

Stage	T_{max}	$\Delta W\%$
1	69.6	9.7
2	298.9	58.1
residue	—	[32.2]

Table 2. The maximum speed of the process (T_{max}) and the mass decrement during the heating process of chitosan-Fc determined from TG and DTG curves

Stage	T_{max}	$\Delta W\%$
1	117.5	8.7
2	253.2	34.0
3	443.6	11.2
4	592.5	2.8
5	736.6	8.6
residue	—	[34.7]

Conclusions

Chitosan derivative with ferrocene was produced in this study. Microwave assisted techniques were applied for the reaction of ferrocenylmethanol with amino groups of chitosan. New procedure for the synthesis of N-ferrocenylmethylchitosan is simple, low cost, safe and time sparing. The FTIR spectrum indicates that the ferrocenyls exist in this biopolymer. Chitosan-ferrocene derivative showed good thermal properties, however different than those for chitosan. Further studies will be perform to find appropriate applications for such derivatives.

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