BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi" din Iaşi
Tomul LIX (LXIII), Fasc. 2, 2013
Secţia
CHIMIE şi INGINERIE CHIMICĂ

CHARACTERISATION OF CHITOSAN MODIFIED BY CARBOXYMETHILATION

BY

DOINA ASANDEI*, ANCA MOISE, GABRIELA LISĂ and ELENA BOBU

"Gheorghe Asachi" Technical University of Iaşi,
Faculty of Chemical Engineering and Environmental Protection

Received: August 15, 2013
Accepted for publication: September 1, 2013

Abstract. Modified chitosan was obtained by the reaction of chitosan and monochloroacetic acid. The characterization of the obtained reaction product was achieved by FT-IR spectroscopy, polarized light microscopy and thermogravimetric analysis. FT-IR spectroscopy confirmed the transformation of chitosan in carboxymethylchitosan by the appearance of specific functional group absorption bands. The results of the thermal degradation of carboxymethylchitosan are consistent with the literature. Polarized light optical microscopy shows that, compared to the chitosan, melting was evidenced for the synthesised carboxymethylchitosan, probably due to the introduction of large lateral group on the hydrocarbon chain. After functionalizing, the melting temperature of chitosan fell slightly below the degradation temperature, which demonstrates its successful derivatization. Modified chitosan has better features for use in cosmetics.

Key words: chitosan, FT-IR, polarized light microscopy, thermogravimetric analysis.

*Corresponding author; *e-mail*: doinacazan@yahoo.com

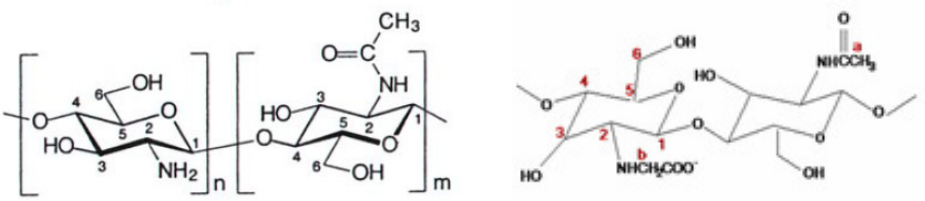
1. Introduction

Chitosan is a polysaccharide, fundamentally a copolymer of N-acetyl glucosamine and glucosamine (Illum & Davis, 2005): poly [β-(1-4)-2-amino-2-deoxy-D-glucopyranose].

Chitosan is obtained by modification of chitin which is extracted from the shells of crustaceans (Kurita, 2001; Vårum & Smidsrød, 2005), and is a natural and inexhaustible source of organic material Desacetylation of chitin may be effected by acid or alkaline hydrolysis in the homogeneous system. (Sannan *et al.,* 1975; Sannan *et al.,* 1976) or heterogenous.

Due to the stable structure (Fig. 1), chitosan is soluble in aqueous solutions with pH less than 7, but in dilute acid media, free amino groups are protonated, it is completely soluble at pH values below 5, solution viscosity is dependent upon the degree of desacetylation, molecular weight, concentration, ionic strength, temperature (Goosen, 1997; Kubota & Shimoda, 2005; Smidsrød & Haug, 1971; Terbojevich *et al.,* 1991).

In order to overcome the main drawbacks of chitosan in various applications, we wanted a chemical modification by carboxymethylation, to confer solubility in water, amphoteric character and retain biocompatibility. Synthesis of N, O- carboxymethylchitosan (Fig. 1 *b*) was conducted by reacting chitosan with monochloroacetic acid under alkaline conditions.



a *b*

Fig. 1 − Structure of chitosan (*a*) (Lim & Hudson, 2003) and Structure of carboxymethylchitosan (*b*).

Chitosan, the most common biopolymer after cellulose, acquires new properties and distinguished by functionalization

2. Experimental

2.1. Materials and Synthesis

Chitosan CHV2 used in the study was produced by Vanson, has numerical molecular weight Mn = 415200, molecular weight gravimetric M_w = 755900, polydispersity index i = 1.82 and degree of acetylation GA = 20.8%.

The rest of the used reagents are analytical reagents: *monochloroacetic acid* as the etherification reagent, *isopropyl alcohol* as the medium reagent and *methanol* to wash the final product.

Soluble chitosan derivative was synthesized under alkaline conditions by reaction of chitosan with monochloroacetic acid. The synthesis involved the following steps (Zhao *et al*., 2002):

− Dispersion of chitosan in isopropyl alcohol to form a suspension;

− Maintaining the chitosan under stirring in the formed alkaline environment by adding a solution of sodium hydroxide at 25°C;

− Adding monochloroacetic acid in a molar ratio determined;

− Raising the reaction temperature from 60° C to fixed;

− The addition of a small amount of water, required for the measurement and correction of pH to pH 7 with glacial acetic acid;

− Filtering and washing the product with 70% methanol under stirring;

− Filtration and redispersion of the product in anhydrous methyl alcohol;

− Filtration and drying the product in an oven for 12 h at 60°C (Ciolacu *et al*., 2003).

2.2. Analysis Methods

The chemical structure of carboxymethylchitosan (CMCTS) was investigated by FT-IR spectroscopy compared to that of chitosan (CTS). The spectra were recorded on a Bio-Rad spectrometer. Digilab FTS 2000 in KBr pellet. Working parameters: 4000-400 cm^{-1} spectral range, no. scans: 24.

Olympus BH-2 polarized light microscope under cross polarizers with a THM 600/HSF9Ihot stage. Working conditions: heating/cooling 20°C/min.

Thermal analyzes were performed using a derivatograph type Mettler Toledo under an atmosphere of nitrogen at a flow rate of 20 mL/min and a heating rate of 15°C/min in the temperature range 25-800°C. Sample weight was 3-4 mg. Operational parameters were kept constant for all samples in order to obtain comparable data. Working curves in order to obtain thermal and kinetic characteristics were performed using software from Mettler Toledo STAR.

3. Results and Discussions

It is noted in CMCTS spectrum as shown in Fig. 2, the appearance of the specific bands absorption to the carboxy group: 1618 peak intense [γ_{asim} (COO)] and 1414 [γ_{sim} COO)] consistent with the results published in the literature (Zhao *et al*., 2002).

Also it is found thar the presence of the absorption bands of the groups (- NH_2, - OH) 3441 cm^{-1} (broad band), -CH_2-(2922 cm^{-1}) (Nada *et al.,* 2006) confirming that the original structure of CTS was not degraded during synthesis and substitution -NH_2 groups is partial. The specific absorption band

of - OH group appears at 3441cm^{-1}, whereas the maximum peak of specific absorption NH_2 group appears at ~ 3100 cm^{-1} (Ardelean *et al.,* 2009).

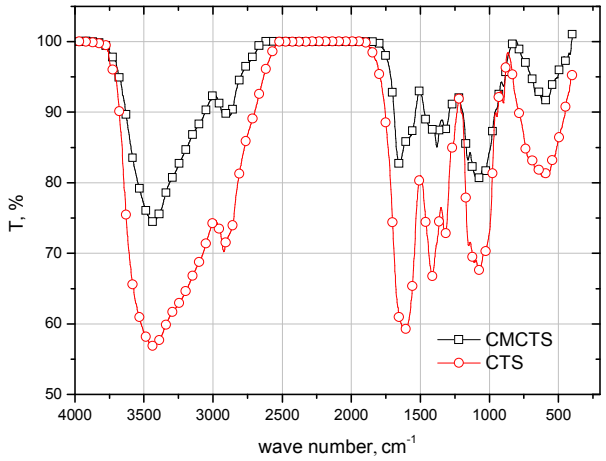


Fig. 2 − FTIR spectra of carboxymethylchitosan and chitosan.

3.1. Polarized Light Microscopy (PLM)

Thermal analyze was realized in polarized light microscopy (PLM) (Marin & Perju, 2009). The chitosan and also the obtained carboxymethylchitosan show a crystalline morphology at the room temperature (Fig. 3). Also, the both samples present thermal decomposition at temperatures of about 250ºC. The visible difference between these two samples (in PLM) is the presence of the phenomenon of melting in the case of CMCTS. At 315ºC, occurs the crystalline melting of CMCTS which is overlapping to the thermal degradation. By comparison, chitosan has not melting, it is rapidly degraded. (Marin *et al.,* 2009).

This fact clearly indicates the structural differences of the two compounds. The carboxymethylchitosan's melting is due most likely because of introduction of large lateral group of chitosan, producing a weakening of the hydrogen bonds between the chains and therefore result in a may loose superstructure (Marin *et al.,* 2011).

Therefore, by functionalizing chitosan its melting temperature lowered to slightly below the degradation temperature, demonstrating its successful derivatization.

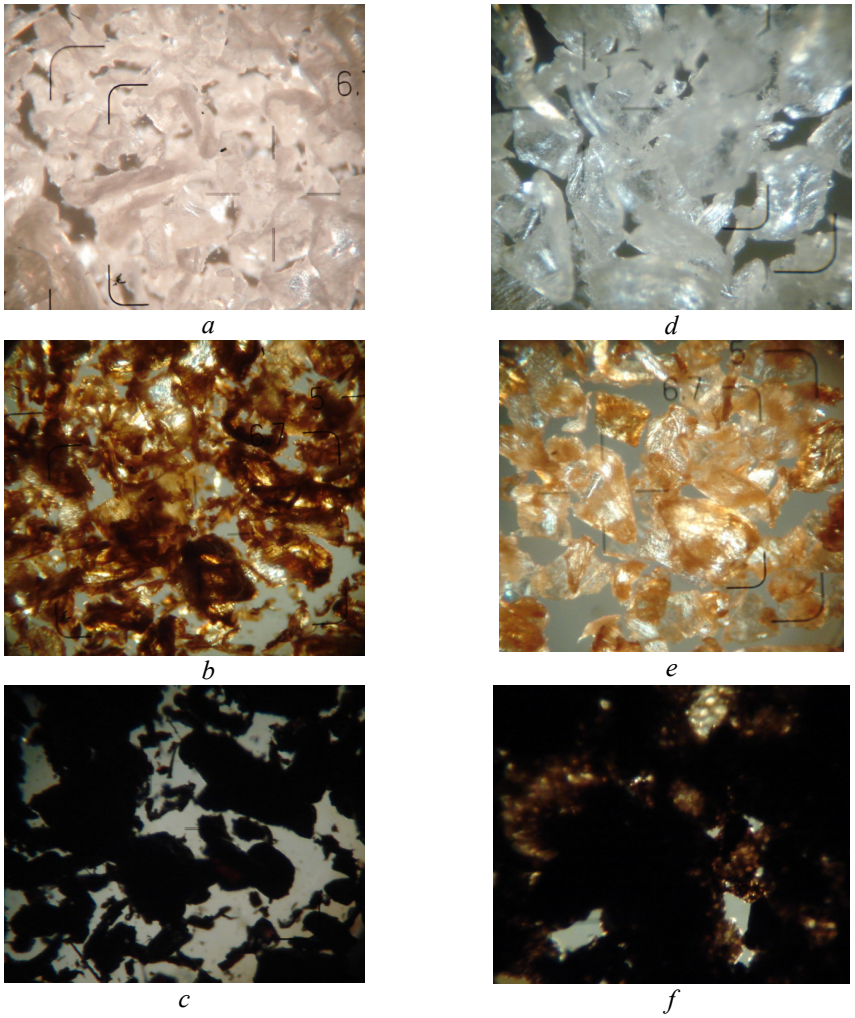


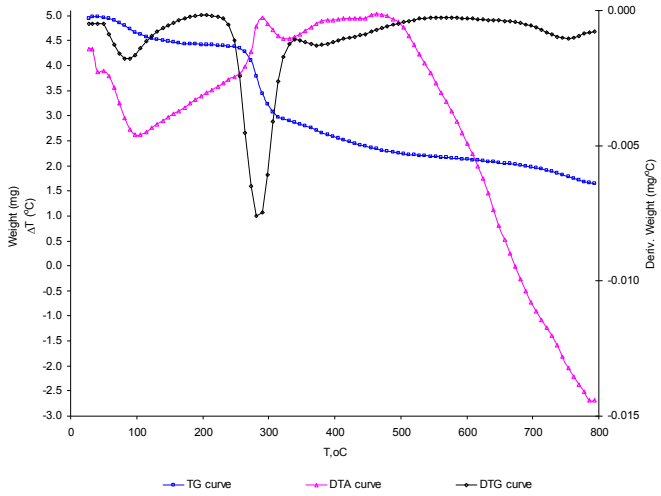
Fig. 3 − Polarized light microscopy: *a* − CTS, RT, 50x, *b* − CTS, 253ºC, 50x, *c* − CTS, 350ºC,50x, *d* − CMCTS, RT, 50x, *e* − CMCTS, 262ºC, 50x, *f* − CMCTS, 315ºC, 50x. [CTS = chitosan; CMCTS = carboxymethylchitosan].

3.2. Thermogravimetric Analysis

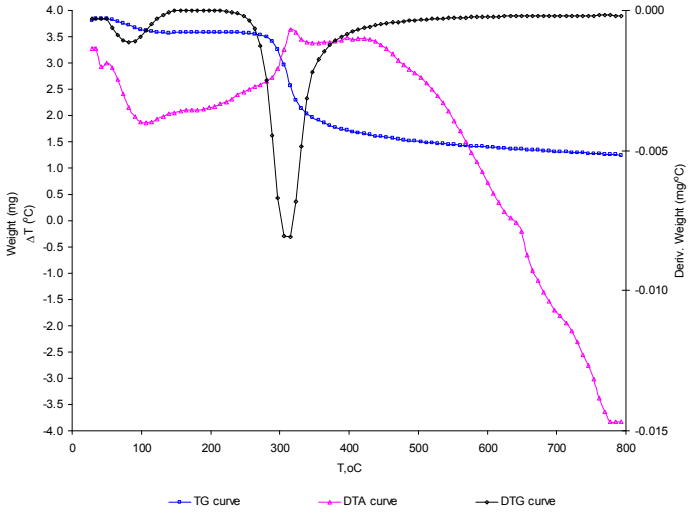
Thermogravimetric curves (TG), derivative thermogravimetry (DTG) and differential thermal (DTA) recorded with Mettler Toledo derivatograph are shown in Fig. 4. It appears that the CMCTS thermal degradation is carried out in four steps and TSA in two stages.

The main thermogravimetric characteristics: T_{onset} − initial temperature when thermal degradation starts at every stage, T_{peak} − the temperature when the

rate of degradation is maximum, T_{endset} − the temperature where the degradation process ends at every stage, W% − percentage of mass loss phase, the characteristic DTA and the amount of residue that remains at a temperature of 800°C are reported in Table 1. The first process that is carried out at temperatures of less than 120°C is associated with the removal of moisture from the samples.



a



b

Fig. 4 − Thermal analysis: *a* − chitosan *b* − carboxymethylchitosan.

Table 1
Thermogravimetric Characteristics

Sample	Step	T_{onset}	T_{peak}	T_{endset}	W%	Characteristic DTA	Residue at 800°C
CTS	I	50	84	111	6.84	endo	31.82
	II	283	311	538	61.34	exo	
CMCTS	I	59	84	157	11.21	endo	32.54
	II	262	285	305	32.38	exo	
	III	305	376	541	14.47	exo	
	IV	697	757	–	9.40	exo	

The main thermogravimetric characteristics shown in Table 1 indicate a good thermal stability both to the control sample (chitosan as CTS) and to carboxymethylchitosan (CMCTS), the thermal decomposition starting at temperature higher than 260°C. Literature (López *et al.,* 2008; Wanjuna *et al*., 2005; de Britto *et al.,* 2007) points out that the initiation of thermal decomposition in an inert atmosphere for chitosan is held in contact C-O-C from about 280°C and it involves depolymerization with the obtain of the monomer, or the formation of acetamide. Carboxymethyl chitosan has a different mechanism of degradation compared to the chitosan, in the temperature range of 260-540°C, distinguish the two phases with peaks at 285 and 376°C. The results of the thermal degradation of carboxymethyl chitosan are consistent with those recently presented by Jiang-Nan Shen (Shen *et al.,* 2013).

4. Conclusions

Chitin and chitosan are natural polymers with many applications. Their linear structure, cationic charge and high molecular weight provide a number of advantages compared with other polymers. Areas of application are, however, limited due to low solubility in water.

To eliminate this disadvantage, chitosan was functionalized by carboxymethylation.

Carboxymethylchitosan produced is not toxic, biodegradable and biocompatible, has antibacterial properties, so it can be used in the areas: food, medical, pharmaceutical, cosmetic.

This study demonstrates the possibility of transforming the chitosan in carboxymethylchitosan by FTIR spectroscopy, polarized light microscopy and thermogravimetric analysis.

Compared with chitosan, carboxymethylchitosan has many advantages in its use in food, medicine and cosmetology due to water solubility.

Acknowledgements. PAPHERCON PROJECT - "Developing Non-conventional Materials and Cold Plasma Technique for Sustainable Solutions in Paper Heritage Conservation" – PN-II-PT-PCCA-2011-3.

REFERENCES

Ardelean E., Nicu (Parpalea) R., Asandei D., Bobu E., *Carboxymethyl – Chitosan as Consolidation Agent for Old Documents on Paper Support, Religious Art Restoration and Conservation.* European Journal of Science and Theology, **5**, *4*, 53−61 (2009).

Ciolacu F., Parpalea, R., Bobu, E., *Carboximetilchitosan – Multifunctional Additive for Papermaking.* Proceedings of the 13th International Symposium on Cellulose Chemistry and Technology, Technical University "Gheorghe Asachi", Iaşi, 192−203 (2003).

de Britto D., Campana-Filho S.P., *Kinetics of the Thermal Degradation of Chitosan.* Thermochimica Acta, **465**, 73–82 (2007).

Goosen M.F.A., *Applications of Chitin and Chitosan.* Technomic Publ. Co., Inc., Lancaster (1997).

Illum L., Davis S.S., *Chitosan as a Delivery System for the Transmucosal Administration of Drugs.* In: *Polysaccharides. Structural Diversity and Functional Versatility*, S. Dumitriu (Ed.), 2nd Ed., Marcel Dekker, New York, 643−660 (2005).

Kubota N., Shimoda K., *Macromolecular Complexes of Chitosan*. In: *Polysaccharides. Structural Diversity and Functional Versatility*, S. Dumitriu (Ed.), 2nd Ed., Marcel Dekker, New York, 679−706 (2005).

Kurita K., *Controlled Functionalization of Polysaccharide Chitin.* Prog. Polym. Sci., **26**, 1921−1971 (2001).

Lim S.H., Hudson S.M., *Review of Chitosan and its Derivatives as Antimicrobial Agents and their Uses as Textile Chemicals*. J. of Macromol. Sci., part C – Polymer Reviews, **2**, 223−269 (2003).

López F.A., Merce A.L.R., Alguacil F.J., López-Delgado A., *A Kinetic Study on the Thermal Behaviour of Chitosan*. Journal of Thermal Analysis and Calorimetry, **91**, *2*, 633–639 (2008).

Marin L., Perju E., Damaceanu M.D., *Designing Thermotropic Liquid Crystalline Polyazomethines Based on Fluorene and/or Oxadiazole Chromophores.* European Polymer Journal, **47**, *6*, 1284–1299 (2011).

Marin L., Destri S., Porzio W., Bertini F., *Synthesis and Characterization of New Azomethine Derivatives Exhibiting Liquid Crystalline Properties*. Liquid Crystals, **36,** *1*, 21–32 (2009).

Marin L., Perju E., *Polysulfone as Polymer Matrix for a Novel Polymer-Dispersed Liquid Crystals System.* Phase Transitions, **82,** *7*, 507–518 (2009).

Nada A.M.A., El-Sakhawy M., Kamel S., Eid M.A.M., Adel Abeer M., *Mechanical and Electrical Properties of Paper Sheets Treated with Chitosan and its Derivatives.* Carbohydrate Polymers, **63,** 113–121 (2006).

Sannan T., Kurita K., Iwakura Y., *Studies on Chitin: 1. Solubility Change by Alkaline Treatment and Film Casting*. Makromol. Chem., *176*, 1191 (1975).

Sannan T., Kurita K., Iwakura Y., *Studies on Chitin: 2. Effect of Deacetilation on Solubility*. Makromol. Chem*., 177*, 3589 (1976).

Shen J.-N., Yu C.-C, Zeng G.-N., van der Bruggen B., *Preparation of a Facilitated Transport Membrane Composed of Carboxymethyl Chitosan and Polyethylenimine for CO_2/N_2 Separation*. Int. J. Mol. Sci., **14**, 3621−3638 (2013).

Smidsrød O., Haug A., *Estimation of the Relative Stiffness of the Molecular Chain in Polyelectrolytes from Measurements of Viscosity of Different Ionic Strength*. Biopolymers, **10**, 1213 (1971).

Terbojevich M., Cosani A., Conio G., Marsano E., Bianchi E., *Chitosan-Chain Rigidity and Mesophase Formation.* Carbohydr. Res., **209**, 251 (1991).

Vårum K.M., Smidsrød O., *Structure – Property Relationship in Chitosan.* In: *Polysaccharides. Structural Diversity and Functional Versatility*, S. Dumitriu (Ed.), 2nd Ed., Marcel Dekker, New York, 625−642 (2005).

Wanjuna T., Cunxinb W., Donghua C., *Kinetic Studies on the Pyrolysis of Chitin and Chitosan.* Polymer Degradation and Stability, **87**, 389−394 (2005).

Zhao Z., Wang Z., Ye N., Wang S., *A Novel N,O-Carboxymethyl Amphoteric Chitosan/Poly(ethersulfone) Composite MF Membrane and its Charged Characteristics.* Desalination, **144,** *1-3* , 35−39 (2002).

CARACTERIZAREA CHITOSANULUI MODIFICAT PRIN CARBOXIMETILARE

(Rezumat)

S-a obţinut chitosan modificat prin reacţia dintre chitosan şi acid monocloroacetic. Caracterizarea produsului de reacţie obţinut s-a realizat prin: spectroscopie FTIR, microscopie în lumină polarizată şi analiză termogravimetrică. Spectroscopia FTIR a fost utilizată pentru a pune în evidenţă transformarea chitosanului în carboximetilchitosan, prin apariţia grupărilor funcţionale specifice. Rezultatele privind degradarea termică a chitosanului carboximetilat sunt în concordanţă cu cele din literatură. Microscopia în lumină polarizată arată că cei doi compuşi au caracteristici diferite, carboximetilchitosanul se topeşte, datorită probabil introducerii grupării laterale voluminoase pe lanţul hidrocarbonat. În urma funcţionalizării chitosanului temperatura de topire a acestuia a coborât puţin sub valoarea temperaturii de degradare, ceea ce demonstrează derivatizarea cu succes a acestuia. Chitosanul modificat are caracteristici mai bune în vederea utilizării în industria cosmetică.