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THERMAL BEHAVIOR OF SCHIFF BASES FROM CHITOSAN

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The thermal behavior of six biopolymeric Schiff bases obtained from the reaction of chitosan and salicylaldehyde derivatives is described. TG curves in air presented three events attributed to water loss, decomposition of the polysaccharide generating a carbonaceous residue that burns at higher temperatures. In N_2 similar results were observed, but the third event is not completed due to the absence of oxidant atmosphere. DSC curves in N_2 showed two events between room temperature and 500°C. The first was attributed to water loss, whereas the second is associated to the decomposition of the polysaccharide. Thermal analysis of biopolymeric Schiff bases showed that the decomposition temperature of C_N and C_{MO} samples increased with temperature which is in connection with the starting chitosan while the samples C_S, C_{Br}, C_{Cl} and C_{ML} started to decompose at similar temperatures compared to the non modified biopolymer.

Keywords: *biopolymeric Schiff bases, chitosan, DSC, TG*

Introduction

Chitosan is the N-deacetylated derivative of chitin, although this N-deacetylation is almost never complete. The presence of aminic groups in the polymeric chain leads to the possibility of several chemical modifications, including the preparation of Schiff bases by reaction with aldehydes and/or ketones [1].

The reaction of chitosan with aromatic aldehydes in acetic acid to produce the corresponding Schiff bases has been described by Tirkistani [2].

Schiff base compounds containing an imine group (–RC=N–), are usually formed by the condensation of a primary amine with an active carbonyl. The interest in such compounds as analytical reagents is increasing, since they enable simple and unexpensive determinations of different organic and inorganic substances [3].

Some papers concerning the thermal behaviour of Schiff bases and chitosan samples have recently been presented in this journal [4–6].

The present work describes the thermal behavior of biopolymeric Schiff bases obtained by the reaction of low molecular mass chitosan (*C*) with salicylaldehyde and five of its substituted derivatives: 5-bromo, 5-chloro, 5-nitro, 5-methyl and 5-methoxy salicylaldehyde. Such substances can be used to improve the properties of chitosan concerning to the chelation of metal ions, production an analytical reagent for determination of metal ions, preparation of modified electrodes, etc.

Here the authors named the biopolymeric Schiff bases to chitosan modified with salicylaldehyde (C_S); 5-nitrosalicylaldehyde (C_N); 5-methylsalicylaldehyde (C_{ML}); 5-methoxysalicylaldehyde (C_{MO}); 5-bromosalicylaldehyde (C_{Br}) and 5-chlorosalicylaldehyde (C_{Cl}).

Experimental

Chitosan with low molecular mass was supplied by Aldrich (44,865-9) and purified according to a previously described procedure [7]. Salicylaldehyde and its 5-nitro, 5-methyl, 5-methoxy, 5-bromo, 5-chloro derivatives were used without additional purification.

Synthesis of the biopolymeric Schiff bases

The biopolymeric Schiff bases were prepared by dissolving the chitosan in 0.1 mol L^{-1} acetic acid. After the complete dissolution, an ethanolic solution of salicylaldehyde was added, and the mixture was kept at room temperature overnight resulting in a yellow hydrogel. The gel was collected by filtration, washed several times with ethanol, and dried in a vacuum oven at 60°C, for 20 h to yield a yellow solid.

Figure 1 presents a generic scheme structure for the chitosan modified with salicylaldehyde and its derivatives.

The characterization of the biopolymeric Schiff bases was performed by IR and ^{1}H NMR spectroscopy. The main results are presented in Table 1. No

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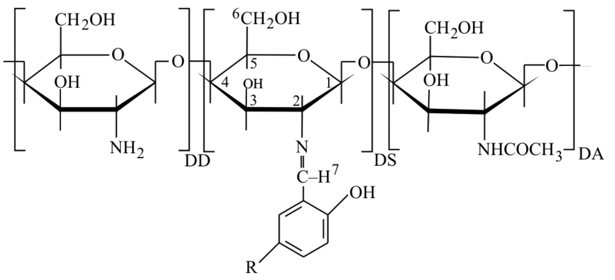

Fig. 1 Generic structure of chitosan modified with salicylaldehydes (*R*=–H, –NO$_2$, –CH$_3$, –CH$_3$O, –Br, –Cl), where $\overline{DD}$=degree of deacetylation, $\overline{DS}$=degree of substitution and $\overline{DA}$=degree of acetylation

evidence of free aldehyde bands were observed in the IR data, except for the C_{MO} derivative.

Thermogravimetric (TG) curves were obtained using TGA-951 thermogravimetric unit coupled to a TGA-2100 thermal analyser, both from TA Instruments, using sample mass of ca. 7 mg and a platinum sample holder under air and N_2 dynamic atmosphere with flowing rate of 100 mL min^{-1}. In all experiments a 10°C min^{-1} heating rate was used.

Differential scanning calorimetry (DSC) measurements were performed in a DSC-910 unit coupled to a TGA-2100 thermal analyser, both from TA Instruments, using sample mass of 3.0 mg in a covered aluminum sample holder with a central pin hole under dynamic nitrogen atmosphere (flow rate=100 mL min^{-1} and heating rate=10°C min^{-1}). Indium metal (99.99±0.01%) has been used to calibrate the DSC module. The sample holders were heated from room temperature to 500°C. An empty pan was used as reference.

Results and discussion

Under nitrogen atmosphere the TG curves (Fig. 2a) presented two mass loss steps for the biopolymeric Schiff bases and chitosan. The mass loss (TG), temperature ranges and a description of thermal events observed in the studies are summarised in Table 2.

For chitosan, the first step showed an initial mass loss of 4.8% between 20.2–203°C, related to the water elimination. The second step occurred between 203–516°C with a mass loss of 53.2%. The decomposition product around 400°C was characterized as a carbonaceous residue, which decomposed slowly from 516°C.

The decomposition temperatures of the second thermal events of the prepared biopolymeric Schiff bases were close to the chitosan's, indicating that they exhibit the same thermal stability the original biopolymer, except C_N and C_{MO}. This is probably due to the effect of the –NO$_2$ and –MeO substituents. In addition, the degree of substitution (Table 3) is not equal for all the samples which makes difficult to compare their thermal stability. The carbonaceous residue decomposes slowly up to the end of the experiment.

Under air (Fig. 2b), after the loss of water, two decomposition steps were observed for chitosan and biopolymeric Schiff bases. The decomposition product around 400°C was characterized as a carbonaceous residue. This residue decomposes in the third step. It can be seen that up to a decomposition temperature the mass loss of the biopolymeric Schiff bases is practically independent of the atmosphere employed. However, the mass losses in air are higher than in nitrogen due to the oxidative decomposition of the residues.

TG curves for the biopolymeric Schiff base also exhibited two events, except the C_{MO} sample that shows three mass loss steps. In case of C_{MO} an additional process was observed between 73–208°C under both air and N_2 atmospheres causing about 8.0% of mass loss. In order to characterize this thermal event the sample was subjected to heat in an oven up to 200°C and the volatile fraction was trapped and was forwarded to GC-MS investigation.

The results showed that 5-methoxysalicylaldehyde is present as the unique component of the volatile fraction. Then the sample was additionally washed with eth-

Table 1 Some relevant IR frequencies and assigments of the signals of ^{1}H NMR spectra

Sample	IR/cm^{-1}			δ/ppm*		
	$\nu_{N–H}$	$\nu_{C=N}$	$\nu_{C=C}$	H-2(D)	H-Ac	H-7
C	3368.9	–	–	3.26(t)	2.05(s)	–
C_S	3457.2	1631.5	1580.9	3.27(t)	2.05(s)	9.97(s)
C_N	3374.9	1640.4	1545.4	3.24(t)	2.05(s)	10.1(s)
C_{ML}	3446.8	1636.6	1590.8	3.25(t)	2.06(s)	9.91(s)
C_{MO}	3448.6	1640.2	1593.7	3.26(t)	2.06(s)	9.95(s)
C_{Br}	3417.9	1633.4	1571.6	3.74(t)	2.57(s)	9.94(s)
C_{Cl}	3426.9	1636.3	1577.7	3.71(t)	2.55(s)	9.98(s)

*for assigments see Fig. 1

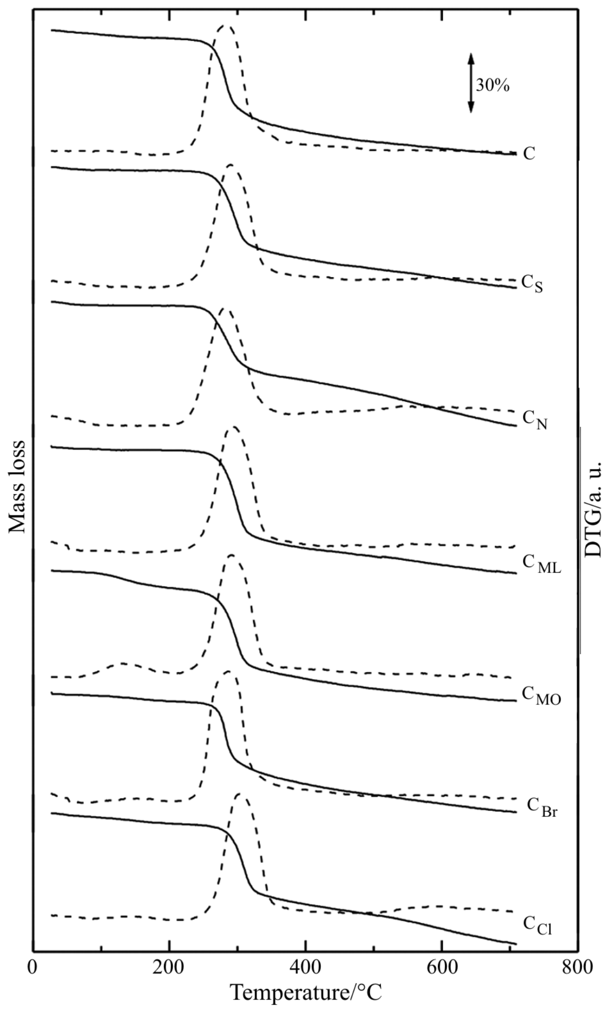

Fig. 2a TG (solid)/DTG (dashed) curves of chitosan and biopolymeric Schiff bases under nitrogen

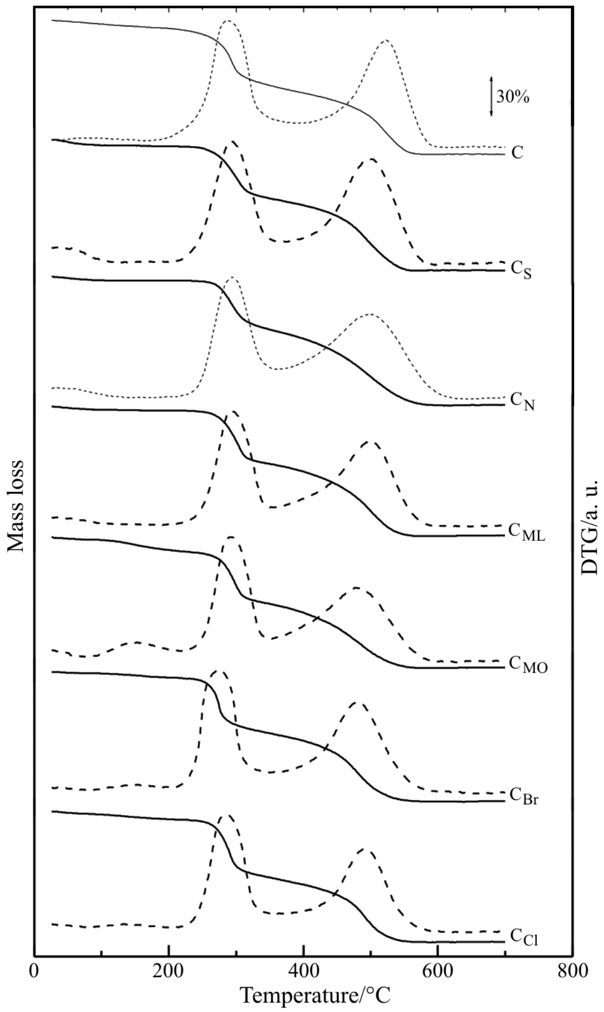

Fig. 2b TG (solid)/DTG (dashed) curves of chitosan and biopolymeric Schiff bases under air

anol several times, and dried again similarly to the original procedure. After then another TG curve was recorded resulting 2% of mass loss between 100–218°C.

It was concluded that the excess of salicylaldehyde is present in the sample, suggesting the occurrence of a strong interaction of this salicylaldehyde derivative with the biopolymeric matrix, which was not observed in the other cases.

DSC curves of chitosan and biopolymeric Schiff bases under N_2 are shown in Fig. 3. They are in agreement with the observations of the TG/DTG measurements.

A broad endothermic peak (Fig. 3) is present in the DSC curves of chitosan around 83°C in N_2 atmosphere related to the loss of water, whereas the exothermic peak at 303°C corresponds to the decomposition of the biopolymer. The biopolymeric Schiff bases presented similar DSC profiles (Fig. 3), but the endothermic peaks were shifted to lower temperatures compared to the chitosan itself. Meanwhile the exothermic peaks were shifted to higher temperatures compared to the pure chitosan, except for the C_{Br} derivative. In agreement with the TG curves this displacement is dependent on the type of substituent in the aromatic ring.

The energy involved in the decomposition step was determined using sigmoidal baseline fitting. It was used to compensate the change in the heat capacity of the sample during transition. The baseline was adjusted by the built-in software for the reacted fraction (α) *vs.* time. Initially, a sigmoidal baseline was drawn from the beginning of the peak to its end. The peak area was normalized by the sample mass to obtain the experimental heat data in J g^{-1} units.

In Table 3 the DSC results are presented obtained under N_2 for chitosan and the biopolymeric Schiff bases.

Table 2 Data taken from the TG/DTG curves corresponding to the dehydration and decomposition of the chitosan and biopolymeric Schiff bases under N_2 and air atmosphere

Process	N_2			Air		
	TR^a/°C	DTG peaks/°C	Mass loss or (residue)/%	TR^a/°C	DTG peaks/°C	Mass loss/%
$CA\cdot nH_2O \rightarrow CA\cdot nH_2O$	20.2–203		4.8	25.1–198		3.4
$CA \rightarrow CR^b$	203–516	280	53.2	198–373	279	46.8
CR^d	516–700		5.0	373–600		48.9
CR	>700		(37.0)	–		–
$C_S\cdot nH_2O \rightarrow C_S + nH_2O$	25.1–203		2.4	23.1–203		5.3
$Q_S \rightarrow CR^b$	203–400	292	46.2	203–346	286	40.2
CR^d	400–700		13.6	346–600		54.0
CR	>700		(37.8)	–		–
$C_N\cdot nH_2O \rightarrow C_N + H_2O$	19.6–220		3.1	18.5–207		3.5
$C_N \rightarrow CR^b$	220–368	282	36.2	207–350	285	38.2
CR^d	368–700		24.5	350–600		56.3
CR	>700		(36.1)	–		–
$C_{ML}\cdot nH_2O \rightarrow C_{ML} + H_2O$	23.4–216		3.1	19.1–201		3.0
$C_{ML} \rightarrow CR^{b*}$	216–435	293	50.4	201–339	286	40.5
CR^d	435–700		12.0	339–600		54.4
CR	>700		(34.4)	–		2.2
$C_{MO}\cdot nH_2O \rightarrow C_{MO} + nH_2O$	19.5–84.5		2.2	19.8–72.7		8.9
$C_{MO} \rightarrow MO^c + C_{MO}$	84.5–207		8.0	72.7–208		
$C_{MO} \rightarrow CR$	207–510	296	51.0	208–333	284	39.3
CR^d	510–700		6.0	333–600		48.9
CR	>700		(33.0)	–		–
$C_{Br}\cdot nH_2O \rightarrow C_{Br} + nH_2O$	20.0–204		4.0	21.1–205		4.8
$C_{Br} \rightarrow CR^b$	204–401	276	47.8	205–340	268	41.5
CR^d	401–700		15.4	340–600		53.4
CR	>700		(32.4)	–		–
$C_{Cl}\cdot nH_2O \rightarrow C_{Cl} + nH_2O$	19.5–207		6.0	19.5–203		6.0
$C_{Cl} \rightarrow CR^b$	207–384	289	45.8	203–346	290	44.2
CR^d	384–700		23.4	346–600		49.5
CR	>700		(24.3)	–		–

^{a}*TR* – temperature range, ^{b}*CR* – carbonaceous residue; ^{c}*MO* – 5-methoxysalicylaldehyde excess;
^{d}*CR* – carbonaceous residue decomposition

The degree of substitution ($\overline{D}\overline{S}$) has been calculated using the areas of the proton in the imine groups (H-7) and the proton of the pyranose ring (H-2) in ^{1}H NMR spectra, as represented by Eq. (1):

$$\overline{D}\overline{S} = \left(\frac{A_{\text{H-7}}}{A_{\text{H-2}}}\right)\cdot 100 \qquad (1)$$

where $\overline{D}\overline{S}$ is the degree of substitution. $A_{\text{H-7}}$, is the area of the peak of proton H-7 and $A_{\text{H-2}}$ is the area of the peak of proton H-2.

The calculated values using Eq. (1) and the ratio between the areas are described above varied from 4.6 to 68.5%, as they are presented in Table 3.

In relation to the effect of substituent on the enthalpy of the decomposition it was observed that the changes are quite similar for the C_S and C_{Cl} derivatives and the original chitosan (C), and this can be related to the low $\overline{D}\overline{S}$ observed in these cases. The C_{Br} modified biopolymer presented a slight increase in the decomposition energy despite its 4.6% degree of substitution.

A remarkable decrease in the decomposition energy have been observed for C_{ML} and C_{MO} modified biopolymers.

However, the most significant effect in the decomposition energy was observed for the C_N modified biopolymer. In this case the presence of the modifier seems to cause a large influence on the decomposition energy of the modified biopolymer, attributed to the inductive and resonance effect of the $-NO_2$ group in the salicylaldehyde ring [8]. The DSC curve of the pure 5-nitrosalicyl aldehyde (5-NS), showed melting peak at 128.8°C and an endothermic one representing the evaporation of the substance at 247.2°C. Since no exothermic peak was observed in the DSC curve of the pure (5-NS), the increase in the decomposition energy in the modified biopolymer can only explained by the presence of the Schiff base in its structure.

Table 3 DSC data corresponding to the dehydration and decomposition of chitosan and biopolymeric Schiff bases under N_2 atmosphere

Process	Temperature range/°C	T_{max}/°C[a]	ΔH/J g^{-1a}	$\overline{DS}^{b}$/%
$C\cdot nH_2O \rightarrow C + nH_2O$	–	83.9±0.1	–	–
$C \rightarrow CR^c$	213–350	303.2±0.1	210.4±2.1 (exo)	–
$C_S\cdot nH_2O \rightarrow C_S + nH_2O$	–	73.9±0.1	–	17.1
$C_S \rightarrow CR^c$	250–350	316.8±0.1	224.5±2.2 (exo)	
$C_N\cdot nH_2O \rightarrow C_N + nH_2O$	–	64.3±0.1	–	19.5
$C_N \rightarrow CR^c$	204–400	314.4±0.1	794.0±7.9 (exo)	
$C_{ML}\cdot nH_2O \rightarrow C_{ML} + nH_2O$	–	63.4±0.1	–	34.1
$C_{ML} \rightarrow CR^c$	198–353	320.0±0.1	199.8±2.0 (exo)	
$C_{MO}\cdot nH_2O \rightarrow C_{MO} + nH_2O$	–	55.1±0.1		68.5
$C_{MO} \rightarrow CR^c$	241–357	318.7±0.1	189.3±1.8 (exo)	
$C_{Br}\cdot nH_2O \rightarrow C_{Br} + nH_2O$	–	60.0±0.1		
$C_{Br} \rightarrow CR^c$	198–327	298.4±0.1	266.9±2.7 (exo)	4.6
$C_{Cl}\cdot nH_2O \rightarrow C_{Cl} + nH_2O$	–	57.3±0.1		
$C_{Cl} \rightarrow CR^c$	154–337	312.4±0.1	227.7±2.2 (exo)	5.3

[a] uncertainties based on three successive runs of samples: ±1% for entalphy and 0.02% in temperature.
[b] $\overline{DS}$ determined by ^{1}H NMR spectroscopy, [c] *CR* – carbonaceous residue

The enthalpies are similar to the chitosan matrix and for C_S and C_{Cl} derivatives; this can be due to the low $\overline{DS}$ observed in these cases. The C_{Br} presented a slight increase in the decomposition energy despite the 4.7% degree of substitution.

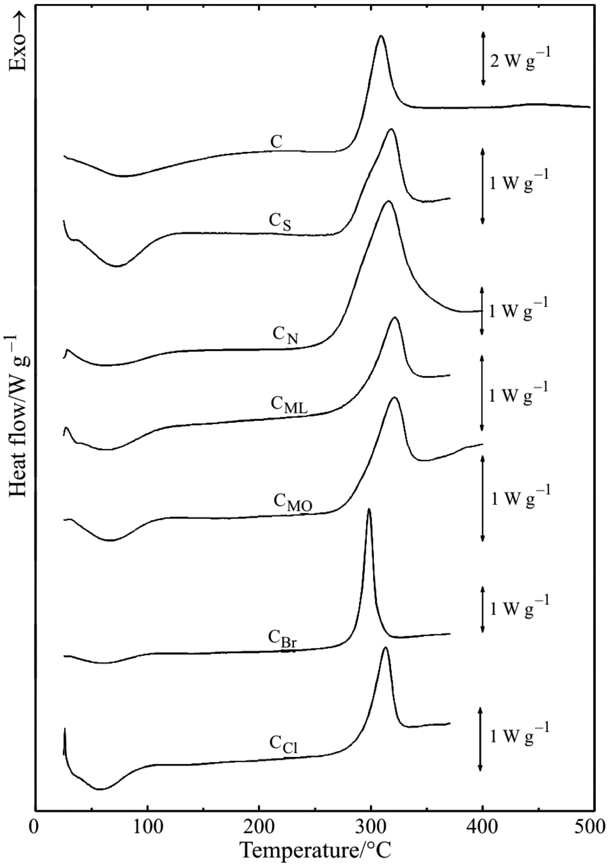

Fig. 3 DSC curves of chitosan (*C*) and biopolymeric Schiff bases (C_S, C_N, C_{ML}, C_{MO}, C_{Br} and C_{Cl}) under nitrogen atmosphere (100 mL min^{-1})

Conclusions

Thermoanalytical methods including DSC and TG can be used as a tool to evaluate the thermal behavior chitosan and biopolymeric Schiff bases. The DSC data indicates that the substituent played an important role in the decomposition enthalpy of chitosan and its Schiff base derivatives.

This study showed that different values of $\overline{DS}$ can be obtained in the preparation of Schiff bases from chitosan. The thermal behavior investigated using TG and DSC revealed that any significative change is observed concerning to the decomposition steps. TG results for C_N and C_{MO} samples suggested an increase in their decomposition temperature.

DSC data showed a considerable effect in the envolved enthalpy on the decomposition of C_N derivative, attributed to the resonance and inductive effect of the modifier.

References

1 M. G. Peter, J. Macromol. Sci. Pure, A32 (1995) 629.
2 F. A. A. Tirkistani, Polym. Degrad. Stabil., 60 (1998) 67.
3 Z. Cimerman, N. Galic and B. Bosner, Anal. Chim. Acta, 343 (1997) 145.
4 A. A. Soliman, J. Therm. Anal. Cal., 63 (2001) 221.

5 F. C. D. Lemos, M. Murano, J. Zukerman-Schpector, É. T. G. Cavalheiro and E. R. Dockal, J. Therm. Anal. Cal., 75 (2004) 599.
6 A. A. Salomé Machado, V. C. A. Martins and A. M. G. Plepis, J. Therm. Anal. Cal., 67 (2002) 491.
7 R. Signini and S. P. Campana-Filho, Polímeros: Ciênc. Tecnol., 11 (2001) 58.
8 T. W. G. Solomons, Organic Chemistry, John Wiley, New York 1992.