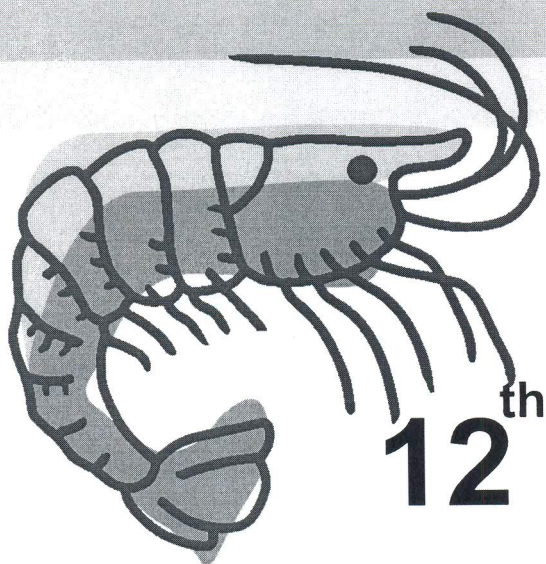




SIAQ

Sociedad Iberoamericana de Quitina



**6<sup>th</sup> Iberoamerican Chitin  
Symposium**

**&**

**12<sup>th</sup> International Conference on  
Chitin and Chitosan**

**VI SIAQ / XII ICC  
September, 02-05, 2012  
Fortaleza / Brazil**



**ABSTRACTS**

**6<sup>th</sup> Iberoamerican Chitin Symposium**  
**&**  
**12<sup>th</sup> International Conference on Chitin and Chitosan**  
**September 2<sup>nd</sup> to 5<sup>th</sup>, 2012**  
**Fortaleza, Brazil**

**Iberoamerican Chitin Society Board**

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### HYDROPHILIC CHARACTERIZATION OF FILMS BASED ON QUATERNARY SALTS OF CHITOSAN

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Chemical modifications were carried out in the polymeric structure of low (LMW) and medium molecular weight (MMW) chitosan. A reductive alkylation in a two-step synthesis was carried out with an initial reaction with appropriate aldehyde. A reducing of the C=N bond was performed by with sodium cyanohydroborate reaction, and a quaternization process by mixing chitosan and alkylated chitosan with dimethylsulfate in an alkaline medium. Details have been described previously [1].

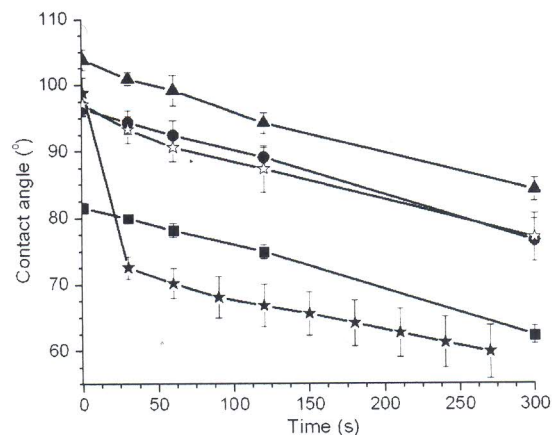
From alkylation reaction N-butylchitosan, N-octylchitosan and N-dodecylchitosan derivatives were obtained, labeled as ButChi, OctChi and DodecChi respectively. The further extensive methylation of the chitosan and the alkyl derivatives via dimethylsulfate route gave the respective quaternary salts: N,N,N-trimethylchitosan, N-butyl-N,N-dimethylchitosan, N-octyl-N,N-dimethylchitosan and N-dodecyl-N,N-dimethylchitosan, identified respectively as TMC, ButDMC, OctDMC and DodecDMC

Derivative polymer solutions were prepared at a concentration of 0.1% w/v and films obtained by casting. The hydrophilic character of the derivatives was estimated by contact angle measurements. The degree of water uptake (swelling) was measured using an immersion assay as described by Möller et al., [2].

The recording water contact angles on films surfaces are shown in Fig. 1. For chitosan and alkylated derivatives the initial contact angles were around 100° for all materials except the ButChi sample (~82°). For all samples a time-dependence behavior was observed of receding angle.

For MMW chitosan the initial contact angle suffer a quickly decreases to approximately 70° in few seconds, attributed to the hydrophilic character of unmodified chitosan. In general, the water contact angle decreases as the extent of surface charge increases and the surface becomes more hydrophilic. Such behavior can be observed to LMW chitosan submitted to neutralization in NaOH (0.1 N), which features more hydrophobically than MMW chitosan. The surfaces however become significantly more hydrophobic when material underwent alkylation. Additionally,

for ButChi, OctChi and DodecChi the values of the contact angle increase in agreement with the increasing hydrophobic character of the respective sequence of 4, 8 and 12 carbons in the alkyl moieties linked to chitosan chain.



**Fig. 1.** Water contact angles variation with time measured on film surface for chitosan and alkylated derivatives: (★) MMW chitosan; (◇) neutralized LMW chitosan; (■) ButChi; (●) OctChi and (▲) DodecChi.

Conversely, for chitosan quaternary salts a significant enhancement of hydrophilicity occurs when compared to the parent sample. For ButDMC salt an average angle reduction of around -15° was measured. For OctDMC and DodecDMC salts the contact angle decreases were less sensible (~ -5°). The greatest reduction in contact angle was observed for the TMC which reached values as lower as 10°, confirming the presence of permanent positive charges in the polymer chains as a generator of a hydrophilic matrix. The degree of swelling, (in ethanol and in water), provides additional information about the hydrophilic characteristics of chitosan and its derivatives, as displayed in Table 1 [3].

**Table 1 - Degree of swelling.**

Sample	DSwt (%)	DSeth (%)
Chitosan	140±5	2±1
ButChi	29±2	70±7
OctChi	98±4	62±9
DodecChi	142±5	3.9±0.5
ChiQt	∞	24±10
ButChiQt	∞	-
OctChiQt	∞	197±13
DodecChiQt	∞	12±2

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