Supporting information for

Interplay between structure and dynamics in chitosan films investigated with solid-state NMR, dynamic mechanical analysis and X-ray diffraction

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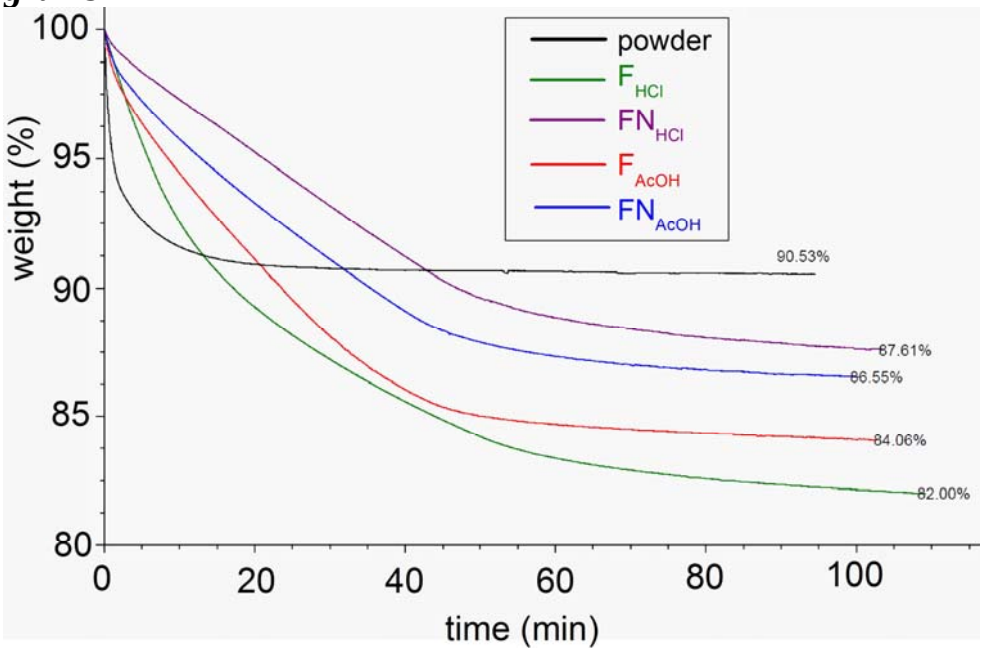
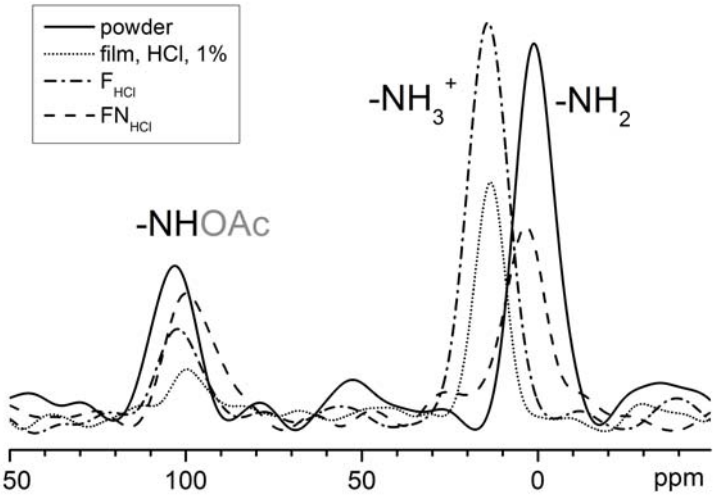
TGA thermograms

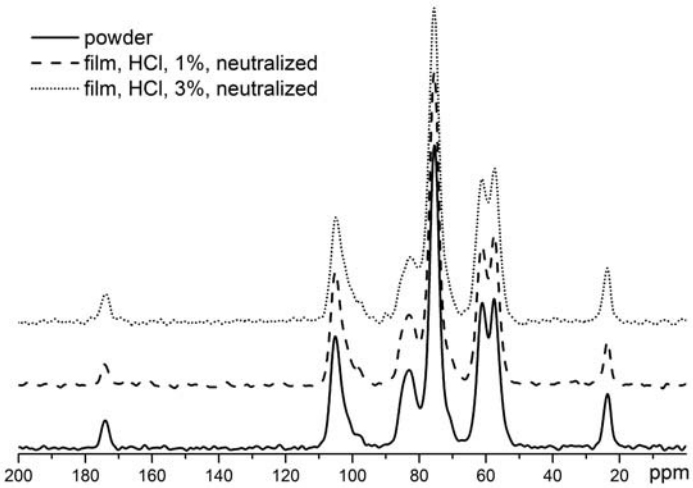


^{15}N CP-MAS NMR spectra

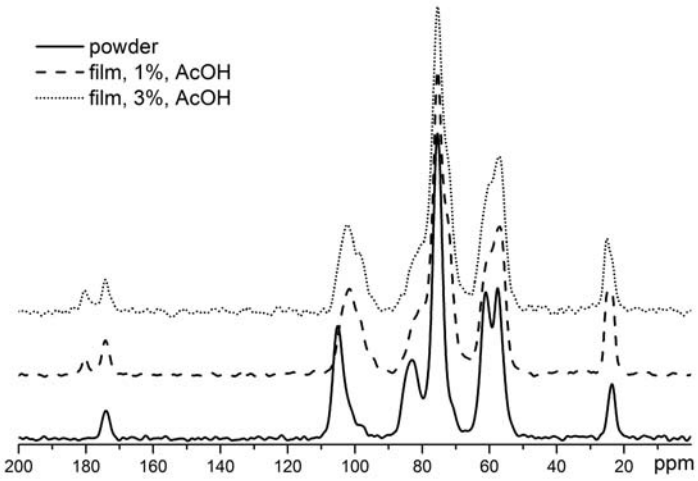


The chitosan concentration (1% or 3%) does not have an influence on the ^{15}N CP-MAS NMR spectrum.

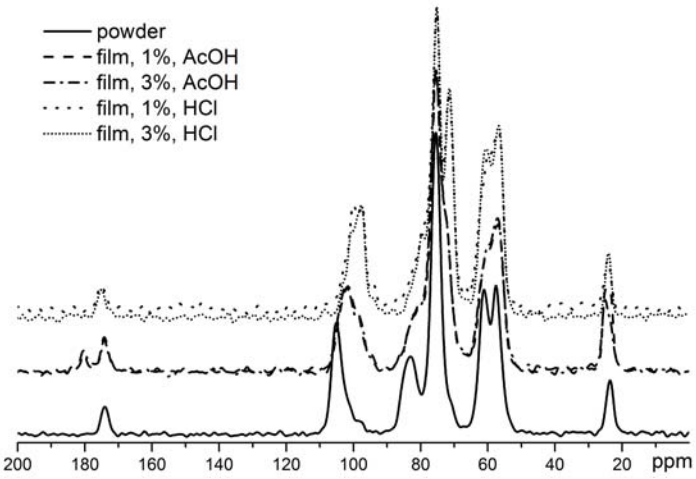
^{13}C CP-MAS NMR spectra



Powder and neutral films all show the same spectrum



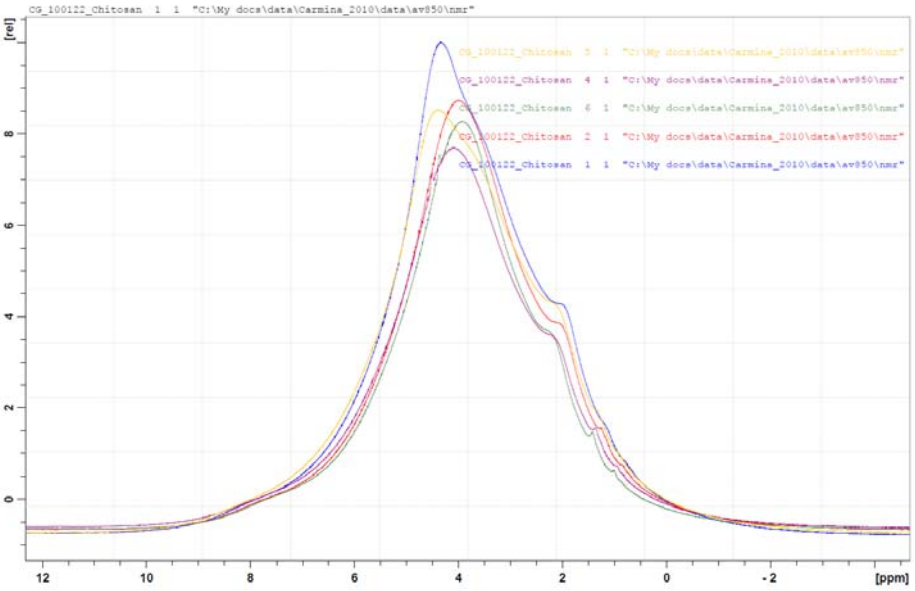
Films prepared in acetic acid show 2 more signals (CH_3 at 25 ppm, C=0 at 180 ppm) due to residual acetic acid.



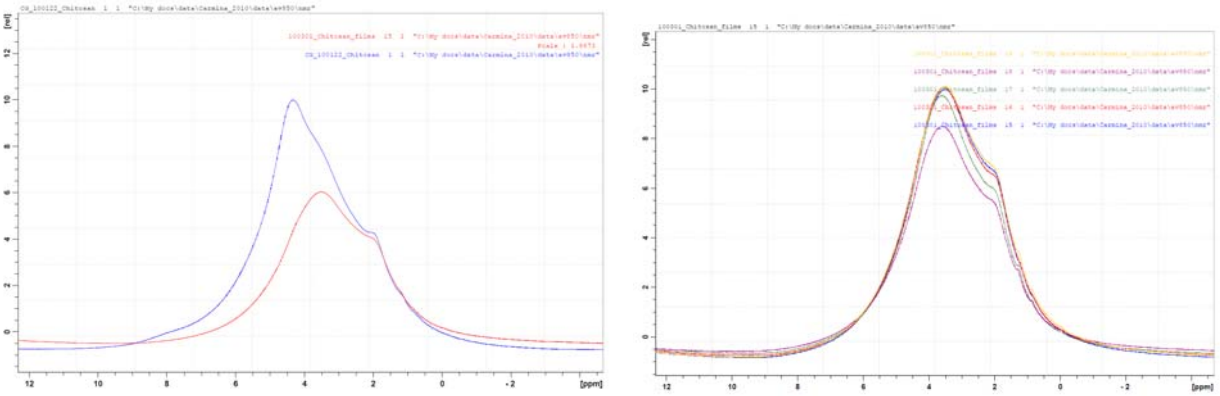
Films which are charged show some signals shift as compared to neutral ones, and these shifts are stronger for films prepared in HCl than in AcOH.

^{1}HMAS NMR spectra

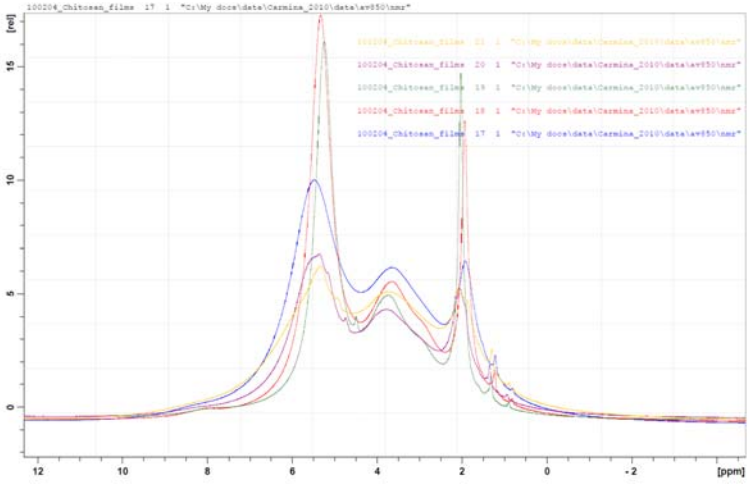
All samples measured at 300, 340, 380, 340, 300 K in that order (blue, red, green, purple then yellow).

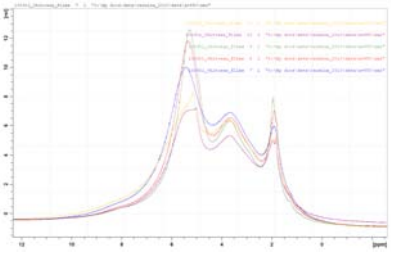


Temperature-dependent ^{1}H MAS spectra of chitosan powder.

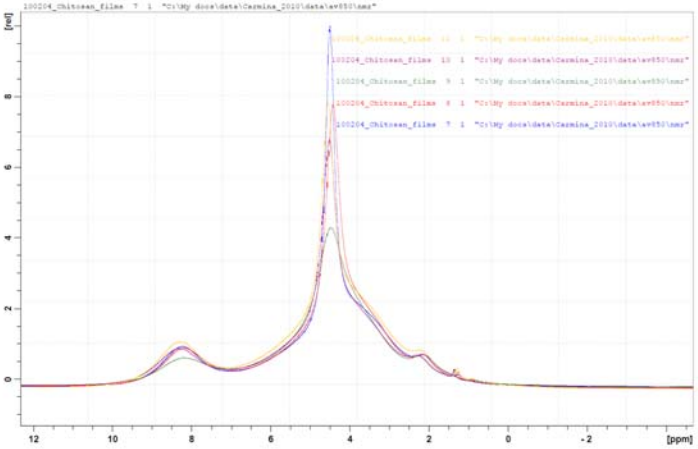


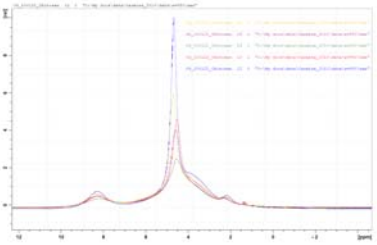
(left) ^{1}H MAS spectra of chitosan powder (blue) and deuterated powder (red). (b) Temperature-dependent ^{1}H MAS spectra of chitosan deuterated powder. The powder was deuterated by suspension in D_2O and freeze-drying, twice.



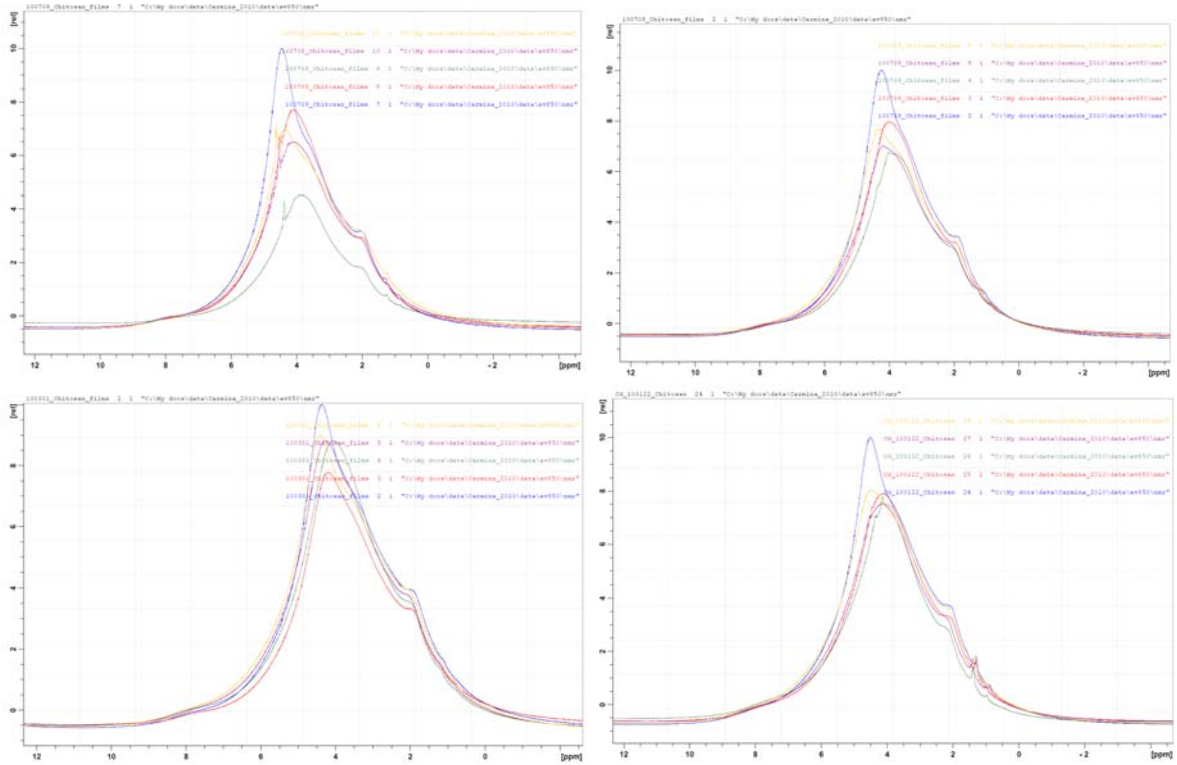


Temperature-dependent ^{1}H MAS spectra of F_{AcOH} (left) and of a film prepared from 1% chitosan in AcOH solution (right).

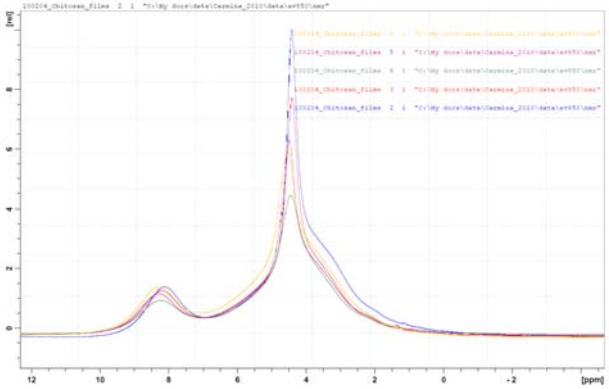




Temperature-dependent ^{1}H MAS spectra of F_{HCl} (left) and of a film prepared from 1% chitosan in HCl solution (right).

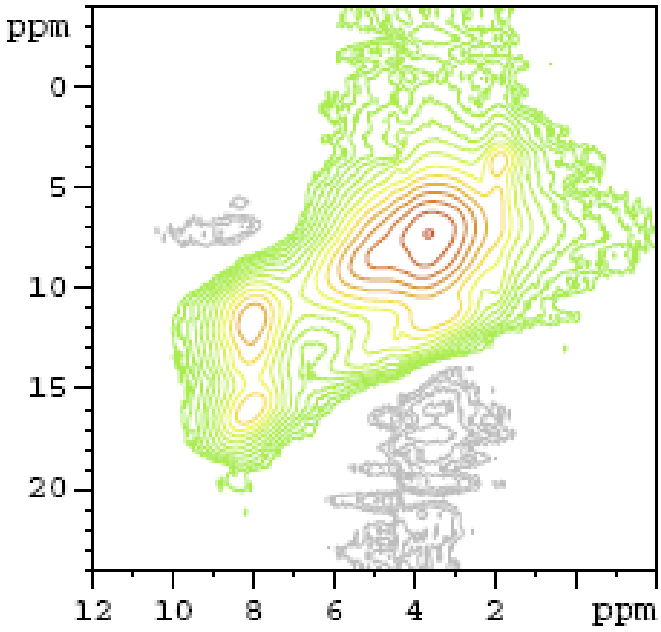


Temperature-dependent ^{1}H MAS spectra of neutralized films: FN_{AcOH} (top left), a film prepared from 1% chitosan in AcOH solution and neutralized (top right), FN_{HCl} (bottom left), a film prepared from 1% chitosan in HCl solution and neutralized (bottom right).

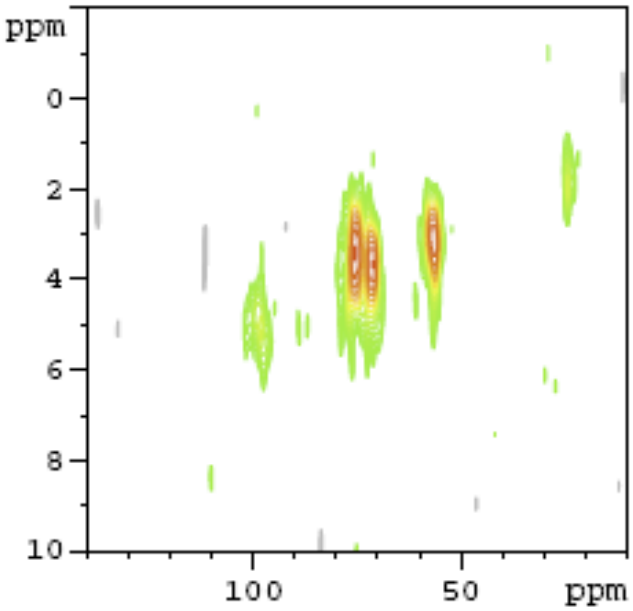


Temperature-dependent ^{1}H MAS spectra of a film prepared from 1% deacetylated chitosan in HCl solution.

Two-dimensional solid-state NMR spectra



Two-dimensional ^{1}H DQ MAS NMR correlation spectrum of a chitosan film prepared from 1% chitosan in HCl solution, recorded with the back-to-back sequence and a recoupling time of 40 μs.



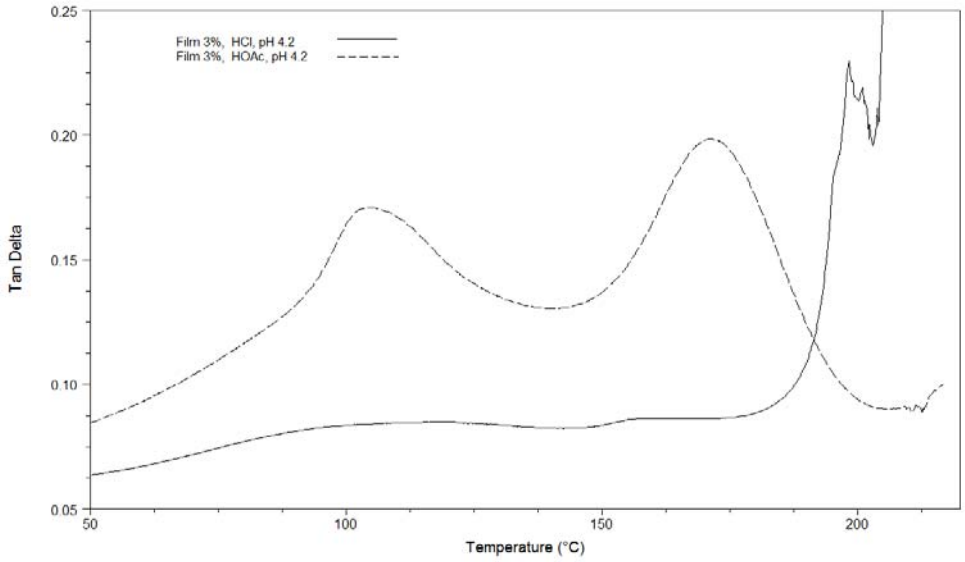
^{1}H-^{13}C HSQC REPT correlation spectrum of a chitosan film prepared from 1% chitosan in HCl solution.

Influence of the pH on the mechanical behavior of the chitosan cast films

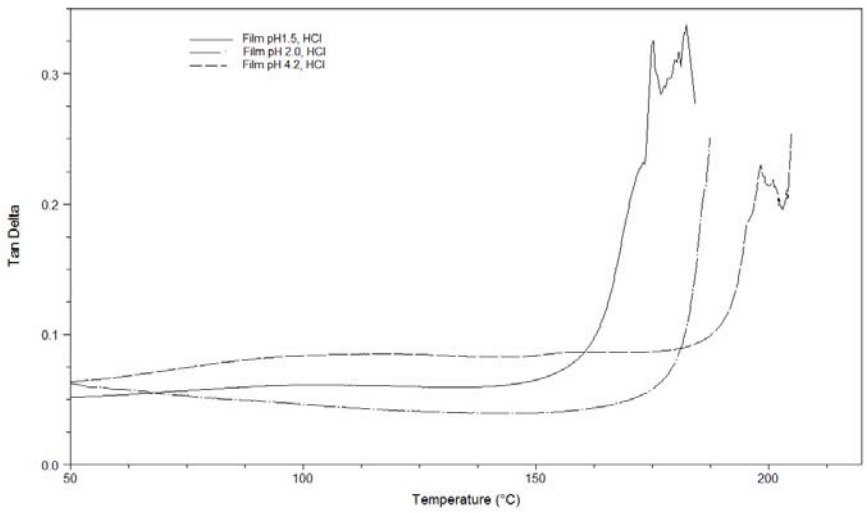
Two films were cast from solutions of 3% w/v chitosan in HCl and acetic acid at the same pH value of 4.2. The mechanical performance of these dry films were measured by DMA (using the same conditions that were reported), to verify if the behavior previously observed depended on the pH of the solution. It is observed in the figure below that the mechanical behavior of both films does not change from what was reported before and that it is independent from the pH. There are two relaxations for the film from AcOH and nearly no observed relaxations for the film from HCl.

Films cast from HCl solutions at pH of 2.0 and 1.5, were also measured by DMA (films were not formed at lower pHs). These films displayed the same mechanical behavior trend. The only difference was a slight change on the onset of the degradation temperature, which is higher at higher pH. These values were 152 °C for pH 1.5, 166 °C for pH 2.0 and 182 °C for pH 4.2.

It can be concluded that of dissociation of the acid as well as the nature of the counterion play a major role in the mechanical properties of chitosan cast films.



Comparison of the DMA thermograms for the films cast from HCl and AcOH solutions at pH 4.2.



Comparison of the DMA thermograms for the films cast from HCl solutions at different pH.

X-ray diffractogram of chitosan powder