Chitosan/Chitin Nanofibrils Plasticized Films studied by means of TGA and DSC

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AIM OF THE PROJECT

Combination of different methods of characterization give a better picture of overall properties of the prepared films.

PREPARATION of BIODEGRADABLE nano-COMPOSITE FILMS from CHITOSAN and CHITIN NANOFIBRILS

Optimization and characterization

- of the **composition** of the slurry,
- of the **preparation procedure** (solution casting)
- choice of the **plasticizer** (i.e. polyglycerols, PEO)
- choice of the **support** …

- ***suitable characterization methods*** (morphology, gas permeability, mechanical, swelling, thermal properties, spectral behavior…)

→ **final possible application in food packaging**

n-chitopack

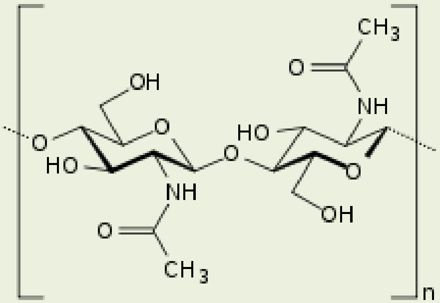
Thermo-analytical Characterization of the Chitosan/Chitin Nanofibrils Plasticized Films

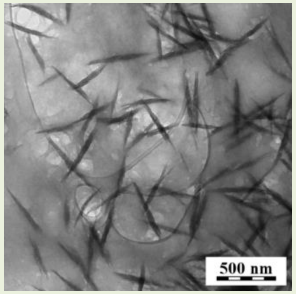
Two rather common thermo-analytical methods, such as TGA and DSC were applied for the composition and behavior characterization of the films.

- ***Thermogravimetric Analysis* (TGA)** → information on the composition of the films via their decomposition patterns: Perkin Elmer TGA Pyris 1, temperature range 30-800 °C, air or N_2, gradual temperature rise of 10 °C/min and gas flow 50 ml/min on samples of about 6 mg.

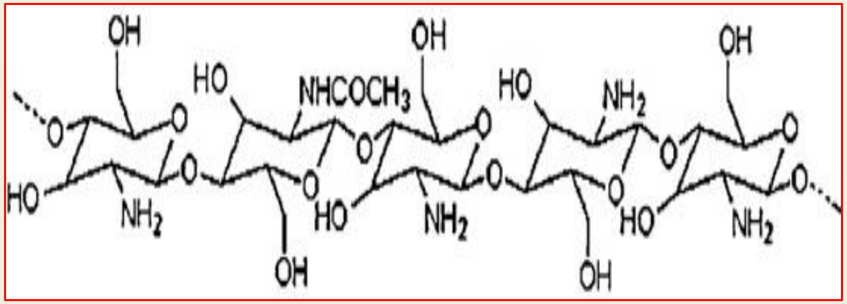
- ***Differential Scanning Calorimetry* (DSC)** → information on the physical parameters (crystallinity, T_g, evaporation, degradation..): Perkin Elmer DSC 8500, temperature range -70 – 200 °C, inert atmosphere of N_2, flow (50 ml/min), temperature rise of 10 °C/min on samples of 2-5 mg.

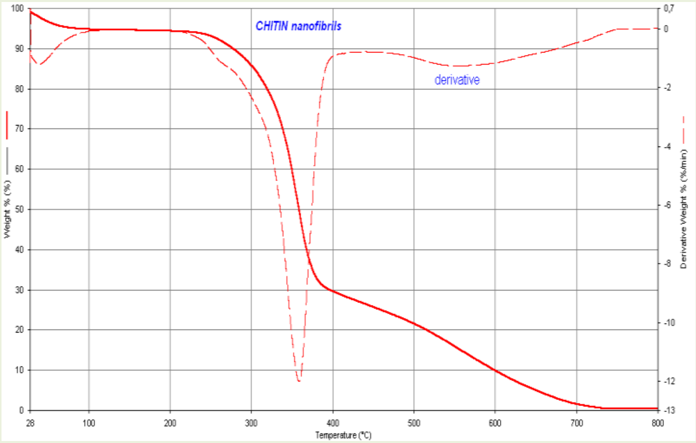
Chitin (CN)/ Chitosan (CS) Films

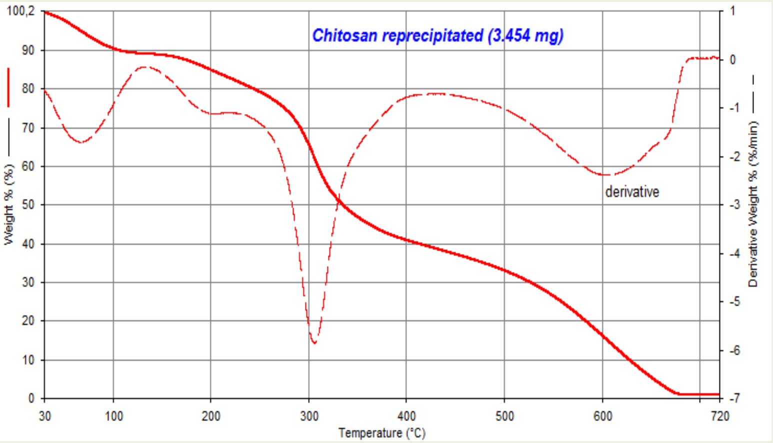




Chitin nano-fibrils



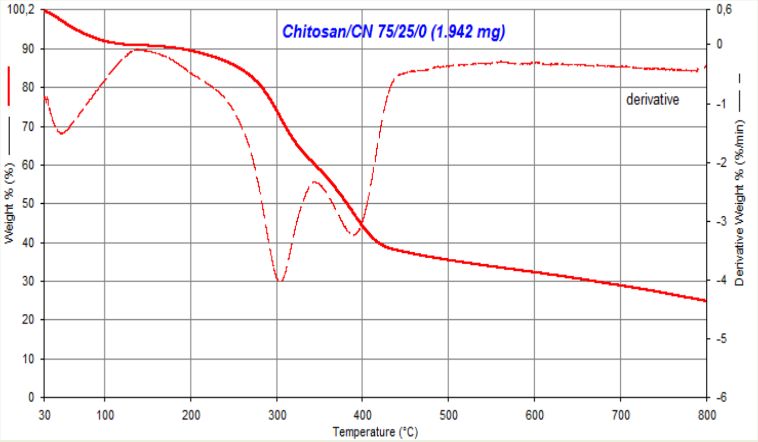


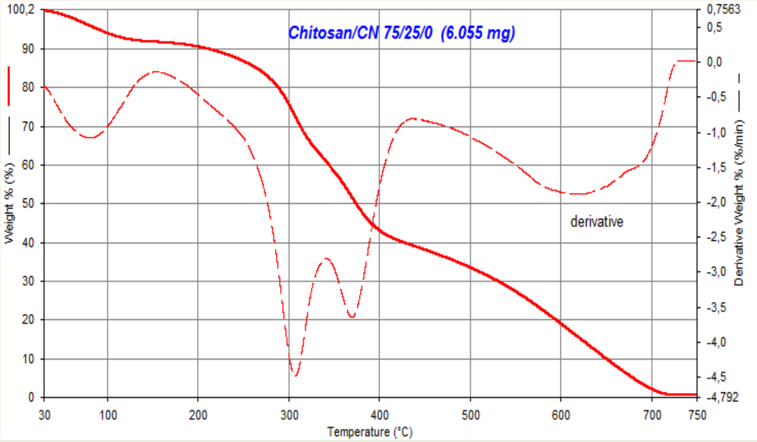


→ Non-trivial mass loss in ***chitin nano-fibrils*** *(5%)* and ***chitosan*** *(12%)* up to 150°C – evaporation of volatiles, mainly water;
→ decomposition of ***chitin nano-fibrils*** started at 230 °C – the highest rate at 360 °C
→ decomposition of ***chitosan*** started around 160 °C – the highest rate at 310 °C

This is an example of the thermal decomposition (TGA curve) of chitin nanofibrils and of reprecipitated chitosan alone. We can see that they both obtain a certain amount of water which evaporates from the start of the measurement.

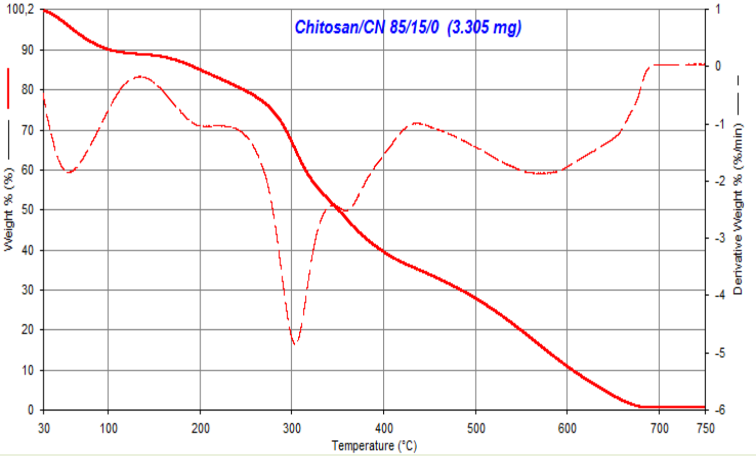
Chitosan/chitin nanofibrils film (various CS/CN ratio wt %)

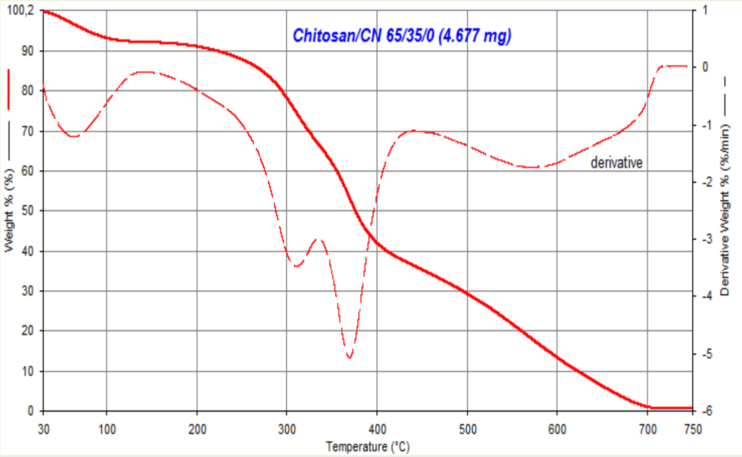




TGA in N_2 → ***char residue 25%***

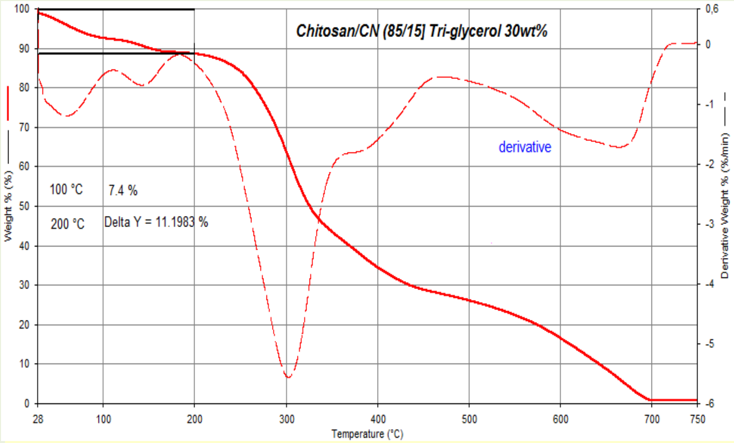
TGA performed in reactive air



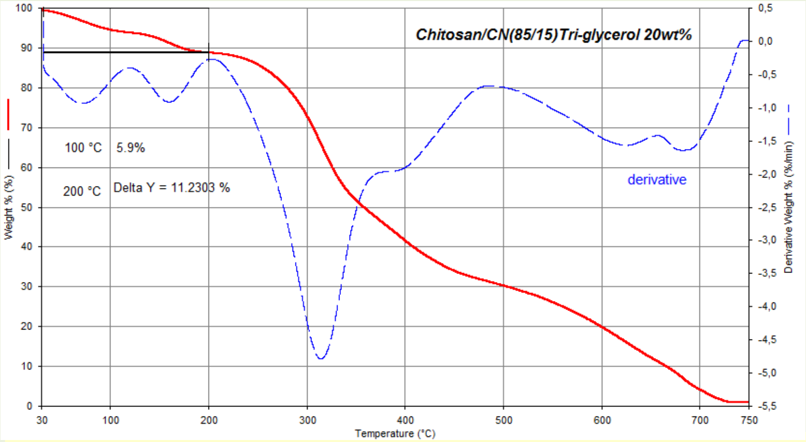


*Possible chitosan chains interactions with chitin nanofibrils → **higher structural order and structural stability** similar to that of chitin*

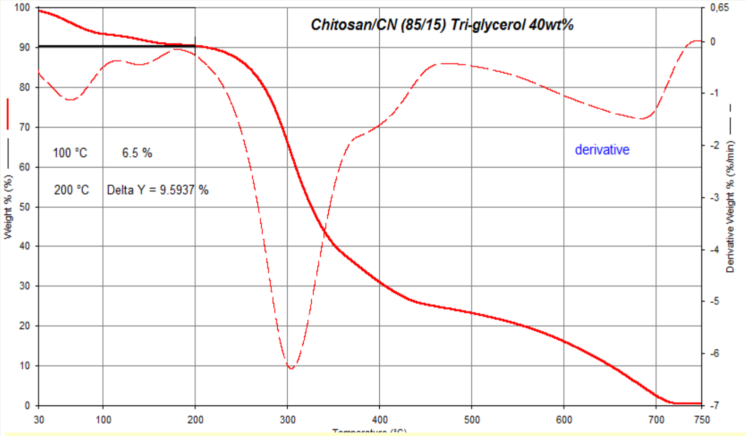
Chitosan/chitin nanofibrils plasticized film



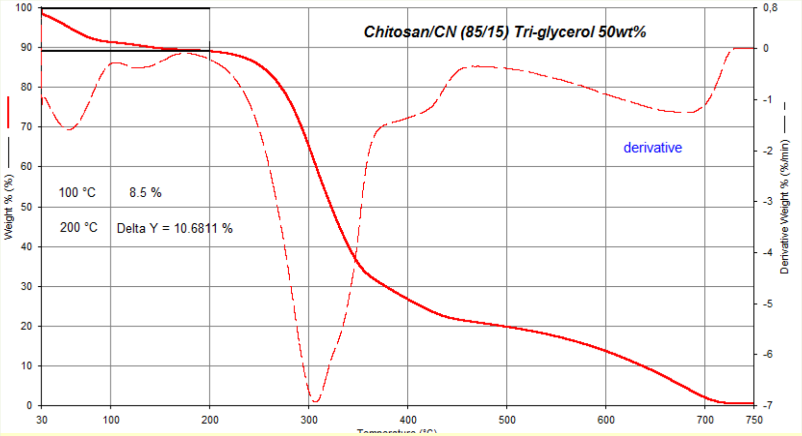
CS/CN (85/15)/30 wt % triglycerol



CS/CN (85/15)/20 wt % triglycerol



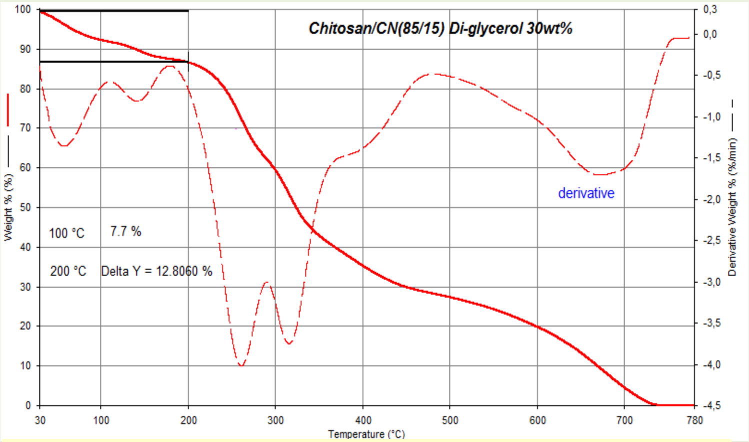
CS/CN (85/15)/40 wt % triglycerol



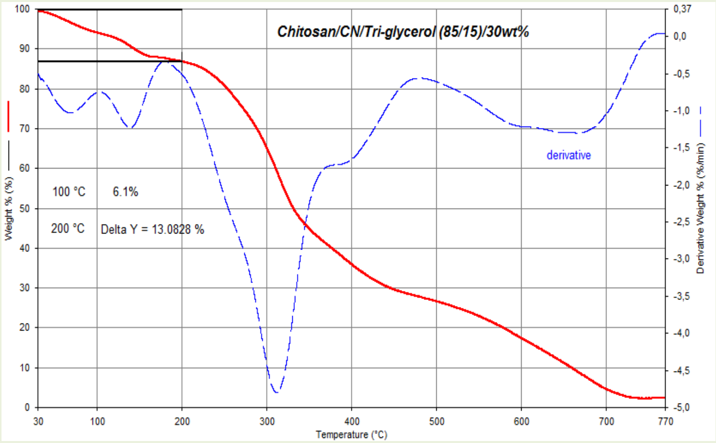
CS/CN (85/15)/50 wt % triglycerol

TGA curves of the films containing varying amounts of tri-glycerol plasticizer are very similar, showing on their derivatives two distinct mass losses at the beginning of the measurements. This behavior confirms good compatibility and plasticizing effect of the applied tri-glycerol.

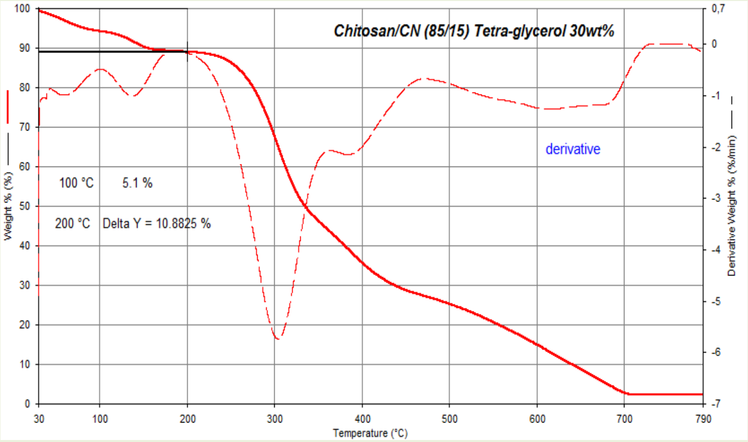
Chitosan/chitin nanofibrils plasticized films (plasticizer 30 wt%)



CS/CN (85/15)/30 wt % diglycerol



CS/CN (85/15)/30 wt % triglycerol



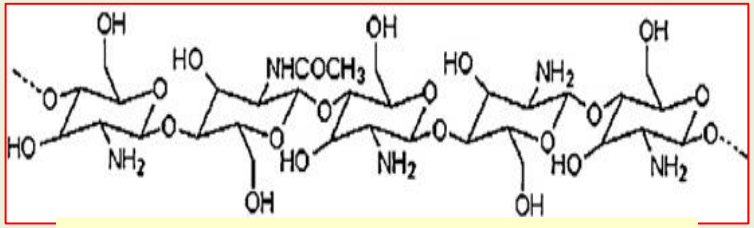
CS/CN (85/15)/30 wt % tetraglycerol

- ***Water content*** **-** binding sites in ***chitosan OH and NH_2 groups***
- ***Polyglycerol plasticizers*** also ***hydrogen bonds interactions*** with chitosan in the plasticized CS/CN films – confirmed also by FTIR.
- ***TGA or FTIR*** not discriminatory techniques

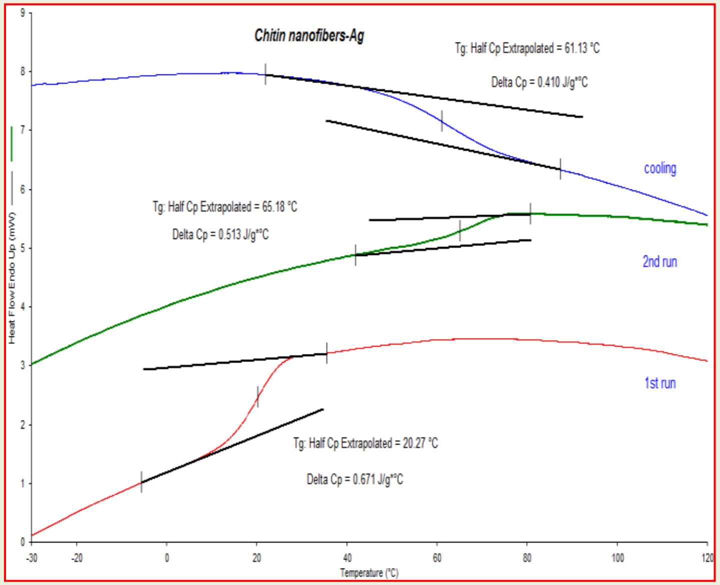
Both water and the applied poly-glycerol plasticizers are competing for the same H-bonds binding sites, like OH or NH_2 in chitosan/CN films.

Chitosan/chitin nanofibrils plasticized film - DSC experiments

- effect of ***water*** loss
- effect of ***plastification*** on T_g values
- effect of sample ***homogenity***
- effect of ***thermal history***



free NH_2 and OH as binding sites



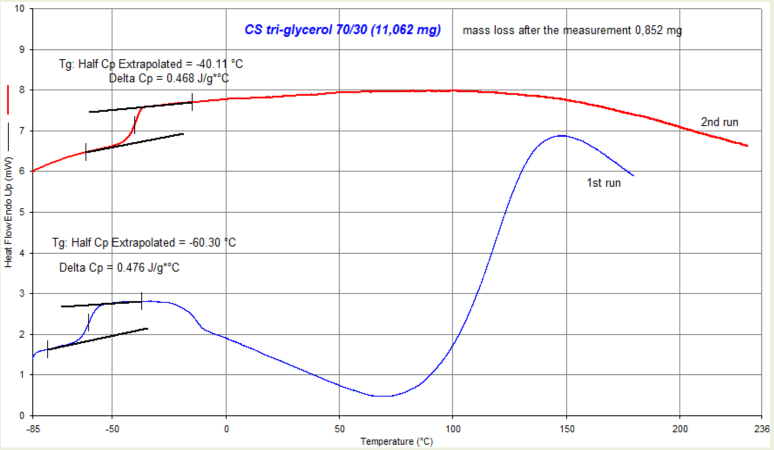
T_g values of Chitin nanofibrils-Ag

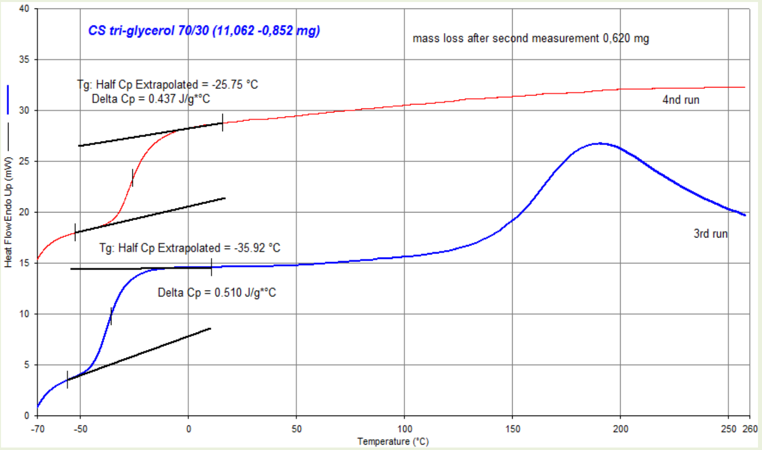
Sample	Triglycerol wt.%	DSC *Tg*,°C 1st run	DSC *Tg*,°C 2nd run	Weight loss after 1st run (%)
Chitin nanofibers (CN) thick film	0	-	-	6.8 (180°C)
Chitin nanofibers-Ag	0	+20.3	+65.2	(150°C)
Chitin nanofibers-Ag	0	-	+107.2	(180°C)
CN thick film	30	-60.2	-37.5	5.7 (180°C)
CN film	30	-61.2	-60.1	0 (50°C)
CN film repeated exper.	30	-56.4	-41.3	(150°C)
Chitosan/CN 85/15	0	+60.7	+ 65.9	33 (200°C)
Chitosan/CN 85/15	20	-32.9 + 0.7	-34.0 +1.0	3.2 (50°C)
Chitosan/CN 85/15	20	-28.5	-18.3	5.1 (80°C)
Chitosan/CN 85/15	30	-31.5	-28.0	0.5 (80°C)
Chitosan/CN 85/15	40	-56.2	-44.9	9.5 (80°C)
Chitosan/CN 85/15	50	-61.5	-49.7	27.0 (80°C)
Chitosan/CN 85/15	30	-19.5	+5.0	17.0 (80°C)
Chitosan/CN 85/15	30	-	-	59.1(80°C)

last two cases – diglycerol and tetraglycerol

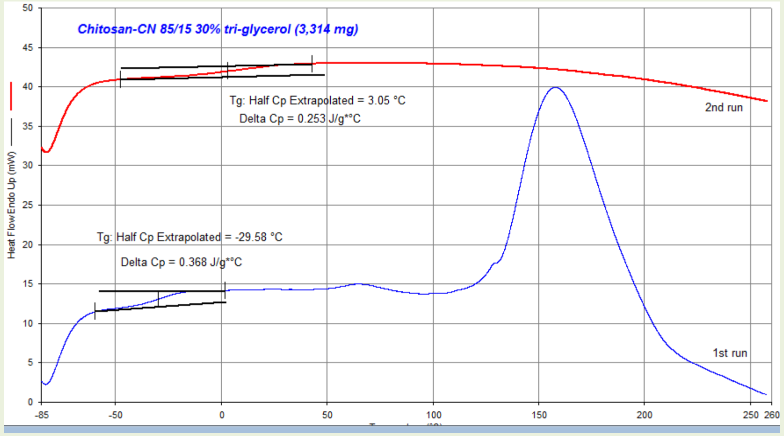
The ever present water content causes a problem in case of DSC measurements because it evaporates on heating the sample in the first run. An example of the shift of the T_g to higher temperature is shown for chitin nanofibrils-Ag in the presented Figure. The results obtained with other measured compositions are shown in the Table, as well as on the following slide.

Chitosan/chitin nanofibrils plasticized film - DSC experiments

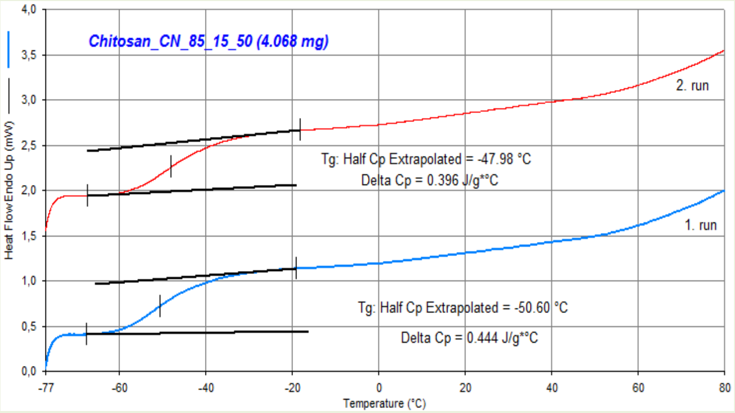




Chitosan-triglycerol(30%) film



CS/CN 85/15-triglycerol(30%) film



CS/CN 85/15-triglycerol(50%) film

CONCLUSIONS

(1) The always present *water* as revealed by TGA experiments affects the properties of the chitosan/chitin nanofibrils films as well as of their plasticized analogs. Free amino and hydroxy groups in chitosan are the most probable binding sites for *H-bonding* .

(2) Water acts as a plasticizer lowering the *T*g of individual components as well as of their composites

(3) To eliminate the effect of moisture *is not easy* .

(4) All polyol plasticizers display interactions with chitosan and CS/CN composites via *H-bonding.*

(5) Various values of *T*g of chitosan or chitin nanofibrils in the literature, i.e. 203, 195, 103, 140-150, 130-139 °C.

(6) Single value of *T*g means miscibility of chitosan/CN composition in the amorphous phase.

(7) A broad water evaporation peak in the vicinity of 100–130°C covers *T*g of water-plasticized chitosan.

Various values of Tg of chitosan or chitin nanofibrils presented in the literature show the complex thermal behavior of the studied films.

Thank you for your kind attention