

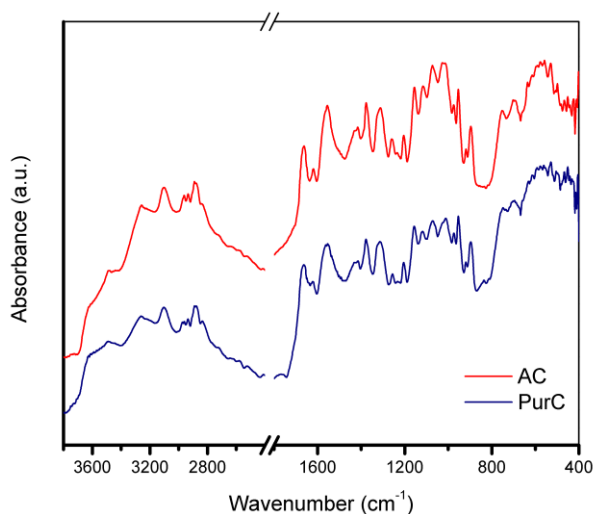
**\*\*Electronic Supplementary Information\*\***

## Green solvent-induced polymorphism in chitin films

Diana G. Ramírez-Wong, Marius Ramírez, Regina Sánchez-Leija, Adriana Rugerio, R. Araceli Mauricio Sánchez, Martín A. Hernández-Landaverde, Arturo Carranza, John A. Pojman, Andrés M. Garay-Tapia, Evgen Prokhorov, Josué D. Mota-Morales\* and Gabriel Luna-Bárcenas\*

### 1. Chitin after the 3-steps purification method: PurC

FT-IR analyses allow us to compare chitin after demineralization and after the 3-steps purification, ESI Fig.1. No major differences are revealed by FTIR spectroscopy, except than a gain in unbound water. However, Fig. 2 shows that PurC is not even dispersible in CCU after stirring and heating. Thus, deproteinization and subsequent bleaching seem to have a negative impact on the solubility of chitin in DES.



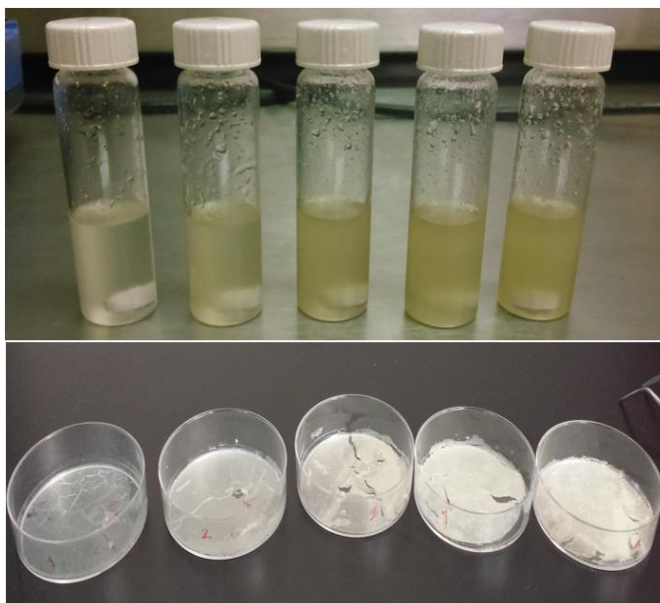
ESI. Fig. 1 FT-IR spectra of purified chitin using the 3-steps method (Pur-C) or by simple acid treatment with HCl 0.25 M (AC).



ESI. Fig. 2 Purified chitin by the 3-steps method (PurC) is neither soluble nor dispersible in CCU.

## 2. Images of chitin dispersions in CCU

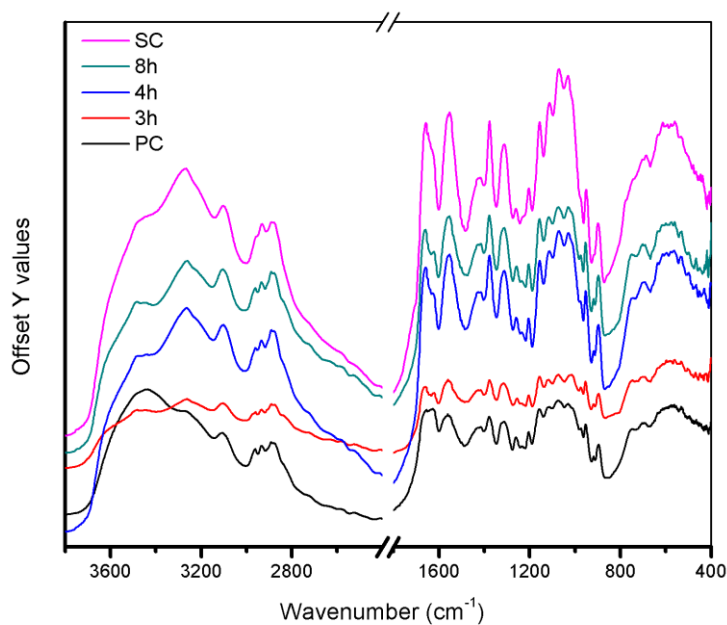
Photograph of different dispersions and films of acid chitin (AC) in CCU DES were taken after 8 hours of continuous stirring at 100° C, ESI Fig.3. The dispersions were kept in storage and no precipitation was observed even after 3 months. The films obtained after precipitation were very fragile at chitin concentrations below 1.0% w/w, which difficult its further manipulation.



ESI. Fig. 3 Dispersions and films of chitin AC in CCU. From left to right (increasing concentrations): 0.5, 1.0, 1.5, 2.0 and 2.5% w/w.

## 3. Chitin demineralization followed by FTIR

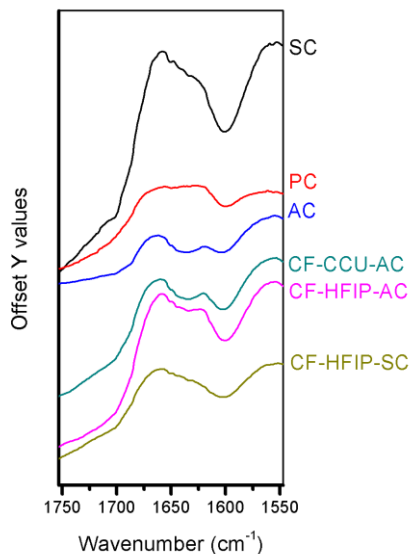
FT-IR analyses allowed us to monitor changes in the fingerprint region (1020–1155  $\text{cm}^{-1}$ ) during acid purification to avoid chitin hydrolysis. The Amide I region (1660–1623  $\text{cm}^{-1}$ ) was also observed and our objective was to achieve a similar profile of the bands of standard chitin (SC).



ESI. Fig. 4 FT-IR spectra of Practical grade chitin (PC), acid treatments at different time intervals (3, 4 and 8 hours) and their comparison against Standard Chitin (SC) of Sigma Aldrich.

#### 4. Amide I region observed by FTIR

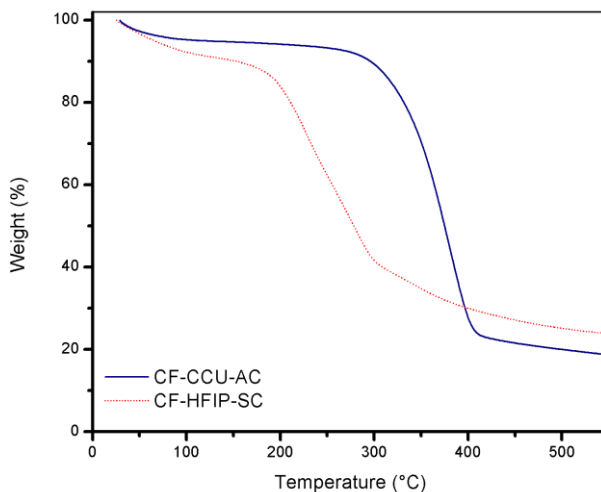
The Amide I region (1660-1623  $\text{cm}^{-1}$ ) is characteristic of chitin structure and essentially exhibits two bands, the first one associated to the occurrence of intermolecular hydrogen bonding and the second one to the intramolecular hydrogen bond. The splitting is clearly observed for the chitin samples that were treated with HCl 0.25 M, but inter- over intra-molecular interactions dominates in all the samples.



ESI. Fig. 5 Amide I region observed by FT-IR for all the samples (powders and films).

#### 5. Thermal stability of chitin films

Chitin films prepared either with the conventional methanesulphonic acid purification and hexafluoroisopropanol (CF-HFIP-SC) or with diluted HCl and CCU DES (CF-CCU-AC) clearly exhibit different thermal stability. CF-HFIP-SC degrades at lower temperatures; while the first loss might be related to a minor content of HFIP (boiling point of 58  $^{\circ}\text{C}$ ), the second and main loss appears below 300  $^{\circ}\text{C}$ . On the other hand, the main weight loss of CF-CCU-AC was observed above 350  $^{\circ}\text{C}$ .



ESI. Fig. 6 Weight loss of chitin films by heating. The continuous line represents the film prepared with acid chitin using CCU DES and dotted red line represents standard chitin films that was dissolved in HFIP.

ESI. Table 1. Summary of thermal stability test for chitin films.

Sample	Mass of Sample [mg]	T <sub>d</sub> 2% [°C]	T <sub>d</sub> 5% [°C]	T <sub>d</sub> 10% [°C]	% H <sub>2</sub> O bound
CF-HFIP-SC	1.3	98.4	165.7	199.1	2.4
CF-CCU-AC	1.9	162.5	282.5	312.4	0.8

## 6. Elemental Analysis

The films CF-CCU-AC, CF-HFIP-SC and their precursors were analyzed to observe all subtle differences of elements present in the films and to track at what step they are incorporated.

ESI. Table 2 shows that the presence of chlorine changes through the process of formation of CF-CCU-AC film. The relative amount of chlorine (Cl) increases after the acid treatment, since the HCl is never fully removed, although we noticed that the percentage of Cl drops after the film is precipitated and rinsed. However, Cl content is never as low as in practical grade chitin, PC. In fact, the percentage of carbon and nitrogen rise from AC to the film in CCU DES, which might indicate the presence of traces of urea and choline chloride in the CF-CCU-AC film.

Most of the data obtained by EDS from CF-CCU-AC and its precursors was limited to the content of C, N, O and Cl; however, traces of metals (like chromium, manganese and iron) and calcium or potassium were also found in AC. Cárdenas et al. have also reported the presence of such metals traces and salts [40].

CF-HFIP-SC was the second film analyzed by EDS. In this case, its precursor -standard chitin (SC)- was purified with methanesulfonic acid (chemical formula CH<sub>4</sub>O<sub>3</sub>S). Therefore, it is reasonable to observe traces of sulfur (S) in SC and also in the film CF-HFIP-SC. The relative amount of C, N, O, S decreases on the film, replaced by 9% of fluorine (F). The use of hexafluoroisopropanol (HFIP) solvent to cast the film seems to be responsible of this fact, since CF-HFIP-SC film was never exposed to temperatures above 70° C, and therefore, HFIP was not fully removed.

ESI. Table 2 Elemental analysis results for the films CF-CCU-AC, CF-HFIP-SC, and their precursors.

	Atom [%]					
	C	N	O	F	S	Cl
PC	55.43 ± 0.11	7.65 ± 0.15	36.88 ± 0.04			0.04 ± 0.001
AC	54.57 ± 0.14	7.49 ± 0.09	37.20 ± 0.16			0.73 ± 0.01
CF-CCU-AC	57.63 ± 0.32	7.96 ± 0.09	34.37 ± 0.36			0.10 ± 0.04
SC	56.58 ± 0.11	7.22 ± 0.19	35.94 ± 0.10		0.26 ± 0.01	
CF-HFIP-SC	51.53 ± 0.04	6.45 ± 0.07	32.81 ± 0.08	9.00 ± 0.14	0.21 ± 0.004	