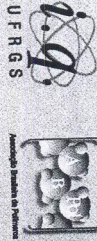


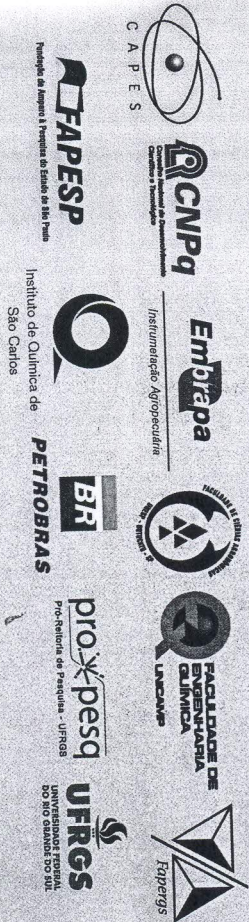
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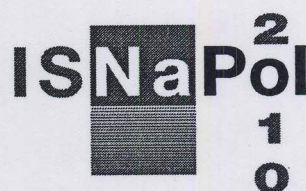
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XII INTERNACIONAL  
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7<sup>th</sup> INTERNATIONAL SYMPOSIUM ON  
NATURAL POLYMERS AND COMPOSITES

## FOREWORD

It is a great pleasure for us to welcome all the participants of the **XII International Macromolecular Colloquium and the 7<sup>th</sup> International Symposium of Natural Polymers and Composites**. We are very pleased with your contributions which are very important to the success of the Meeting. During this time, researchers will have the opportunity to initiate and enhance fruitful interactions among different institutions around the world working in the field of Polymer Science and Technology. We hope this Meeting will also offer a good opportunity to improve the research on the field of natural polymer-based materials and composites developed in Brazil.

Without your participation and specially the contribution of those presenting the 30 lectures, 34 oral sessions and 411 posters it would not be possible to organize this Meeting. We would like to acknowledge also the support from BRASKEM, CAPES, CNPq, FAPERGS, FAPESP, Petrobras and PROPESQ-UFRGS and the participation of the exhibitors dpUnion, Instrutécnica, Polimate and Reoterm.

We wish all the participants lots of interesting discussions and important stimulus for their further work and a pleasant stay in Gramado.

Organizing Committee





# CHITOSAN/PECTIN BLENDS: INFLUENCE OF THE IONIC INTERACTIONS ON PROPERTIES IN THE SOLUTION AND SOLID STATES

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Juliano E. de Oliveira<sup>1,2</sup>, Francys K. V. Moreira<sup>1,2</sup>, José M. Marconini<sup>2</sup>, Luiz H. C. Mattoso<sup>2,\*</sup>

1 – Programa de Pós-Graduação em Ciência e Engenharia de Materiais, PPG-CEM, UFSCar – julianoufmg@yahoo.com.br; moreira.fkv@gmail.com; 2 – Laboratório Nacional de Nanotecnologia Aplicada ao Agronegócio, LNNA – Embrapa Instrumentação Agropecuária, CNPDIA, Rua XV de Novembro, 1452, 13560-970, São Carlos/SP - marconini@cnpdia.embrapa.br, \*mattoso@cnpdia.embrapa.br

In the current work, biodegradable chitosan/pectin blends were prepared by mixture of polymers in acetic acid solutions. The influence of interactions of protonated amine groups in chitosan and carboxylate groups in pectin on rheological behavior in the liquid state, as well as solid state, was evaluated by several techniques. The results showed that polyelectrolyte complexes were formed by electrostatic interactions between chitosan and pectin groups, changing the polymeric solutions from Newtonian to a pseudoplastic flow behavior. The infrared spectra of the blend films have showed modification in the typical bands of chemical groups, evidencing chemical interaction in the solid state. As consequence, synergistic effects on water affinity and mechanical properties were observed for blends. The chitosan/pectin blends developed in this work show superior properties when compared with neat polymer films allowing to explore new applications of chitosan and pectin for biomedical, agricultural and food packaging devices.

## Introduction

Development of natural polymer-containing systems is an important route for to introduction of new materials and technologies in modern-day, where concepts such as non-toxicity and biodegradability have become increasingly important. These concepts have motivated academic and industrial research to develop novel materials labelled as “eco-friendly” especially natural polymers obtained from agro resources [1].

Pectin (PEC) is a biodegradable, renewable and anionic natural polymer with complex structure, consisting mainly of poly( $\alpha$ -(1 $\rightarrow$ 4)-D-galacturonic acid segments chain whose carboxylic units are partially esterified with methanol (called methyl-esterification degree, DM) [2], Figure 1a. PEC is the major component of the residues from agribusiness citrus fruit, notably in Brazil, one of the largest producers of orange juice in the world.

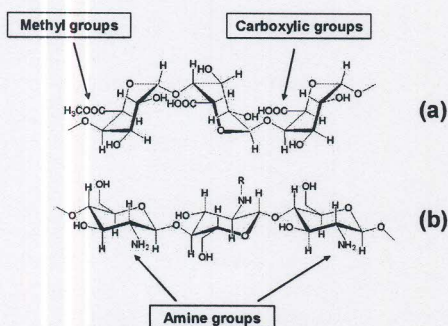


Figure 1: Molecular Structure of (a) pectin and (b) chitosan.

In order to improve some of the undesirable properties of PEC, polymer blending with cationic polymers may also offer an opportunity to elaborate various materials and explore some of their interesting new properties. Chitosan (CHT), Figure 1b, is the deacetylated form of chitin and is comprised of  $\beta$ -(1,4)-2-deoxy-2-amino-D-glucopiranosose and partially  $\beta$ -(1,4)-2-deoxy-2-acetamide-D-glucopiranosose monomer units with mainly primary amine functional groups [3]. Chitosan has been found to be non-toxic, biodegradable, biofunctional, biocompatible and was reported by several researchers to have strong antimicrobial and antifungal activities [4]. In addition, CHT is a soluble polycation under pH < 6 and has been used extensively to prepare ionically crosslinked hydrogels with anionic polymers, including alginate, arabic gum and pectin [5-7]. Generally, the formation and degree of specific intermolecular interactions between PEC and CHT is responsible for observed mixing behaviors of the blends prepared from aqueous solutions and can reflect on the final properties of the blend in the solid state. The understanding of these correlations is therefore of importance to explore further applications of CHT/PEC blends for biomedical, agricultural and food packaging devices.

The principal aim of this work was to prepare CHT/PEC blends and demonstrate that specific chemical interactions between these natural polymers give new properties for the final materials. The results are discussed with base in rheological analysis of blend



solutions and morphological, spectroscopic and mechanical characterization of blend films.

## Experimental

### Materials

Chitosan (low molecular weight, 20-300 cP, 75-85% deacetylated) was obtained from Sigma-Aldrich (Steinheim, Germany). Standardised low methoxyl pectin (DM = 8,4%) was acquired from CPKelco (Limeira, Brazil). All of the other chemicals were of analytical grade and were used without additional purification.

### Blends Preparation

Chitosan (CHT) and pectin (PEC) blends were prepared by solution blending through use of PEC and CHT solutions at 0,5 % (w/w) in acetic acid solution 1 % (v/v). After filtration step, these two solutions were mixture in the CHT/PEC proportions of 75/25, 50/50 and 25/75 (w/w) at 12000 RPM for 30 min. For complete evaporation of solvent and obtain blend films a mass of 380 g of each blend solution was cast into a Teflon support and dried at 35 °C for 20 h. Pure CHT and PEC were prepared in the same way. All materials were conditioned at 40-60 % RH for further characterizations.

### Zeta Potential, Aggregate Size

Polymeric aggregate size (mean diameter) and zeta potential were determined by photon correlation spectroscopy (PCS) and electrophoretic mobility, respectively, using a Malvern spectrometer Nano-ZS (Malvern Instruments, UK). Each solution was analyzed in triplicate with 3 readings for sample suspended in distilled water. Measurements were carried out at 25°C.

### Rheological Characterization of Blend Solutions

Viscoelastic properties of the polymer blends were measured with a MCR 301 rheometer (Paar Physica, Messtechnik, Stuttgart, Germany) at 35 °C. Truncated cone-plate geometry (1°, 75 mm diameter) was used, in which the truncated cone had a gap of 0.05 mm between the flat surfaces of both elements. First, the viscosity of the polymeric solutions was carried out at 10-150 s<sup>-1</sup> shear rate. Afterwards, oscillatory single frequency time sweep curves were carried out at constant angular frequency and strain deformation of 10 rad s<sup>-1</sup> and 1%, respectively, until constant elastic modulus (*G'*) was achieved. Each sample had a characteristic time to achieve constant *G'*, and samples were left to stand after their loading into the rheometer for this period of time to allow their structure recovery. The amplitude strain (0.01–100%) sweeps were determined at an angular frequency ( $\omega$ ) of 10 rad s<sup>-1</sup> in order to determine the linear viscoelastic region, i.e., the curve region where the dynamic storage modulus (*G'*) and loss modulus (*G''*) are independent of strain.

The oscillating sweep measurements were carried out over an extended angular frequency ( $\omega$ ) domain of 500–0.1 rad s<sup>-1</sup>. All the measurements were done by duplicate, and their means were reported.

### Scanning Electron Microscopy (SEM)

Film samples were cut and fixed onto specimen supports to obtain surface images. After gold coating procedure, micrographs were registered in magnification of 3000x using a Zeiss DSM 960 microscope operated in the secondary electron mode and accelerating voltage of 17kV.

### FT-IR Vibrational Spectroscopy

The FT spectra were obtained on a Nicolet 470 Nexus spectrometer in transmission mode using a thick film obtained by drop casting of polymers supported on a silicon wafer. A total of 64 scans were collected with a resolution of 2 cm<sup>-1</sup> for each sample.

### Mechanical Tests

The mechanical property tensile strength (TS) (MPa) for films was determined from stress-strain curves obtained according to ATSM D882-09 [8] using a universal test machine EMIC DL-3000 with a 50kN load cell. Five specimens 10x1cm were utilized to determinate the average value of this property.

## Results and Discussion

### Blend Solutions

In order to investigate the effect of chitosan ratio on blend solutions prepared by mixed CHT in PEC solutions, a series of experiments were carried out. The obtained blend solutions were examined by dynamic light scattering (DLS) as shown in Figure 2a.

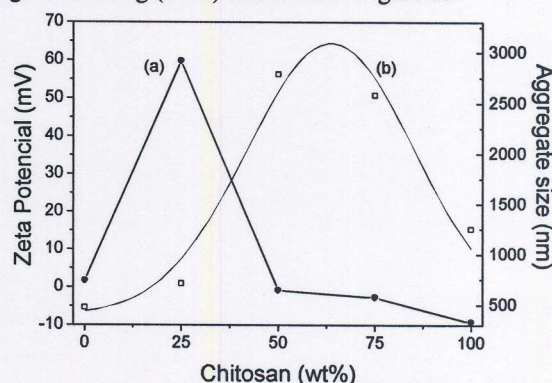


Figure 2: Effect of chitosan ratio in size (a) and zeta potential (b) of the CHT/PEC blend.

From these results, it can be seen that, the diameter of the polymeric aggregates increases from 300nm (PEC 100) to 3000nm (CHT/PEC 25/75).

This result depends of the nature of the interactions involved in the blend formation, which is predominantly electrostatic, as indicated by zeta



potential in the Figure 2b. The blend formed as a result of a cross-linking between chitosan and pectin. The cationic characteristic of chitosan is a crucial parameter for the complex formation. In the CHT/PEC 25/75 sample the zeta potential is approximately null. This result is related with the ratio of cationic groups in chitosan and anionic groups in pectin.

The purpose of the rheological characterization is to present some experimental results on rheological properties of solutions of chitosan and pectin. It is predict that chitosan can form ionic complexes with pectin due to strong bonds between carboxylate groups in pectin and protoned amine groups in chitosan [9, 10]. Such interactions can help to form miscible blends these natural polymers. The rheograms in Figure 3 show the viscosity as a function of shear rate for pure polymer solutions as well as blend compositions.

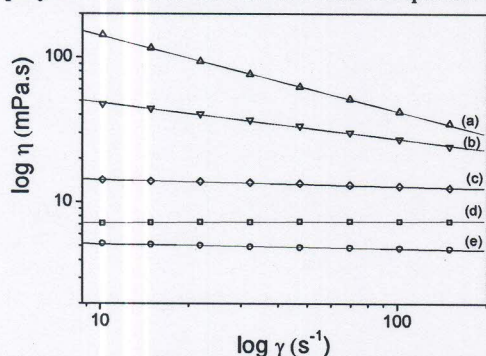


Figure 3. Log shear viscosity versus log shear rate of: (a) CHT/PEC 25/75; (b) CHT/PEC 50/50; (c) CHT/PEC 75/25; (d) CHT; (e) PEC.

All curves have been plotted over a log-log scale with shear rate ranging from  $10 \text{ s}^{-1}$  -  $150 \text{ s}^{-1}$ . It was observed that the flow and viscosity curves are straight lines indicating that the Carreau equation (Power law model) is a suitable model for the representation of the data [11, 12]. A decrease in the viscosity of the blend solution and progressive decrease of the shear viscosity with the increase of weight fraction of chitosan was observed, while the flow curves for pure polymer solutions reflect a Newtonian behavior. A pseudoplastic behavior was observed in blend solutions. However, looking more precisely one can notice a positive deviation (from additivity) of shear viscosity of the system only in the case of presence of a small amount of chitosan in the pectin solution, which can be explained just by the highly level of complex formation between chitosan and pectin.

The consistency (K) and power law (n) index obtained were in the Table 1. CHT and PEC solutions used in the present study are nearly Newtonian ( $n \approx 1$ ). It was observed that blend compositions between 0-25w% of CHT exhibit a non-Newtonian behaviour with pseudoplasticity increasing with pectin concentration (Figure 3). Considering the values of n obtained, the blend with 25% wt of chitosan is highly pseudoplastic in nature with its power law index as 0.48, evidencing deviation from Newtonian behaviour due to the presence of ionic cross-linking.

Table 1: Flow parameters of solutions

Chitosan Ratio	Power Law Index	Consistency Index
0	0,97	0,01
25	0,48	0,47
50	0,75	0,09
75	0,95	0,02
100	0,99	0,01

A decrease in viscosity with increasing shear rate has usually been assumed to be due to a reduction in the extent of three dimensional network structure in the polyelectrolyte systems. Most gels based on these systems are indeed shear sensitive. Therefore, the aggregate size increases in the polymer blends in accordance with our observations from the zeta size (Fig.2b). Such conclusion is not very obvious for the polyelectrolyte complexes because the Newtonian regime has not been attained. However, for all studied systems the viscosity increases with increase of the pectin in the blend.

Figure 4 shows the pure polyelectrolyte solutions which has high frequency dependence of both  $G'$  and  $G''$

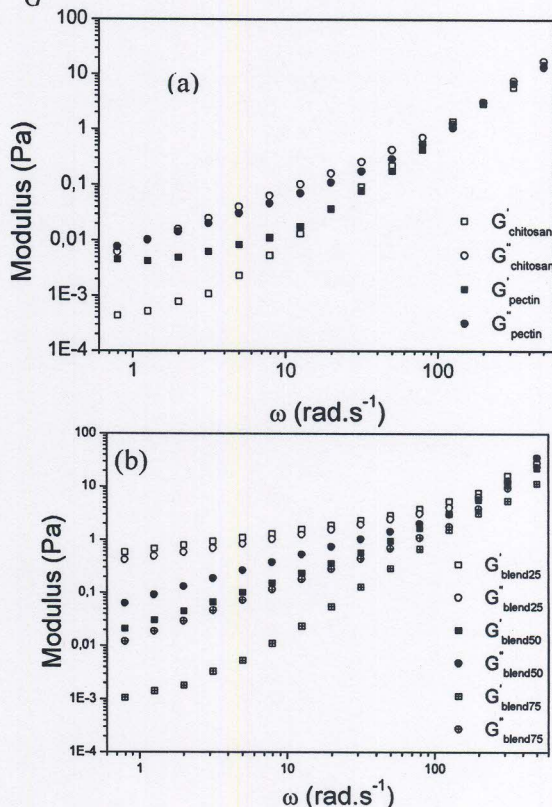


Figure 4. Frequency dependencies of  $G'$  and  $G''$ , obtained from oscillatory rheological measurements for (a) pure polymers and (b) blend systems

The crossover frequency for these solutions is about 80 Hz. In the curves of complex solutions (50 and 25wt% of chitosan), the crossover frequency up to 125 Hz. However, in the complexes a weak gel-like system is



obtained with a high-frequency dependence of  $G'$  and  $G''$  up to the crossover frequency. Beyond that, both modulus show a progressive increase with the frequency and no plateau value is obtained. Similar behavior of both modulus is observed with the complex formation. The addition of lower amount of chitosan (chitosan 25% wt) results in a weak gel-like system where  $G'$  is always higher than  $G''$ . Both modulus are highly frequency dependent and increase in a parallel manner with increasing frequency of oscillation. No crossover frequency could be obtained for this complex.

We must note that the polymer charges are in excess (in 50 and 75% wt chitosan). Therefore, the lowest chitosan concentration used in our work, 25% wt chitosan, formed in terms of charge density a neutral complex system. This is reasonable since the strong electrostatic interaction between pectin and chitosan causes precipitation when the concentration of pectin in complex is increase. This result is compatible with potential zeta plot (Fig.2b).

#### Blend Films

The examination of the surface of CHT, PEC and CHT/PEC blend films was carried out using SEM. Micrographs in Figure 5 showed compact structure and uniform surfaces for pure films, but PEC film surface is smoother than CHT one. The blending process of CHT and PEC resulted in a homogeneous and rather smooth surface as illustrated for micrograph of CHT/PEC blend 50/50.

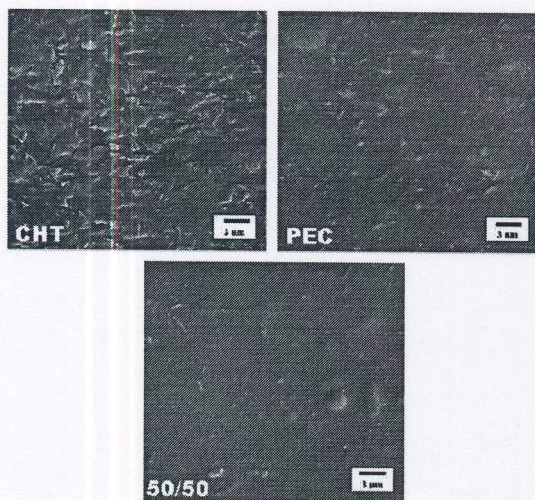


Figure 5: SEM micrographs for CHT, PEC and CHT/PEC blend 50/50 in magnification of 3000x.

FT-IR spectra, Figure 6, were recorded in order to evaluate possible interactions, in state solid, among chemical groups of the PEC and CHT. The FT-IR spectrum of CHT showed a broad and intense O-H stretching band  $\nu(\text{OH})$  at  $3453 \text{ cm}^{-1}$ . It overlaps the band at  $3365 \text{ cm}^{-1}$ , which was attributed in this study to the N-H stretching  $\nu(\text{NH})$ , and overlaps the C-H

stretching  $\nu(\text{CH})$  band between  $2930$  and  $2850 \text{ cm}^{-1}$ . CHT displayed two strong vibrations bands in the regions between  $1700$  and  $1500 \text{ cm}^{-1}$ : at  $1653 \text{ cm}^{-1}$  due to combination of C=O stretching of amide I  $\nu(\text{C=O})_{\text{COON}}$  and asymmetric deformation of  $\text{NH}_3^+$   $\delta_{\text{as}}(\text{NH}_3^+)$  bands and at  $1590 \text{ cm}^{-1}$  assigned to combination of  $\nu(\text{C=O})_{\text{COON}}$  of amide II, N-H bending mode and symmetric deformation of  $\text{NH}_3$   $\delta_{\text{s}}(\text{NH}_3^+)$  [5]. The FT-IR spectrum of PEC displayed typical  $\nu(\text{OH})$  and  $\nu(\text{CH})$  bands at  $3438 \text{ cm}^{-1}$  and  $2935 \text{ cm}^{-1}$ , respectively, besides a intense band at  $1746 \text{ cm}^{-1}$  attributed to the C=O stretching of carboxylic  $\nu(\text{C=O})_{\text{COOH}}$  and esters  $\nu(\text{C=O})_{\text{COOR}}$  groups. In addition, two vibrational bands were observed for carboxylic groups of PEC in your carboxylate form: asymmetric stretching  $\nu_{\text{as}}(\text{C=O})_{\text{COO}^-}$  at  $1616 \text{ cm}^{-1}$  and symmetric stretching  $\nu_{\text{s}}(\text{C=O})_{\text{COO}^-}$  at  $1442 \text{ cm}^{-1}$  [13].

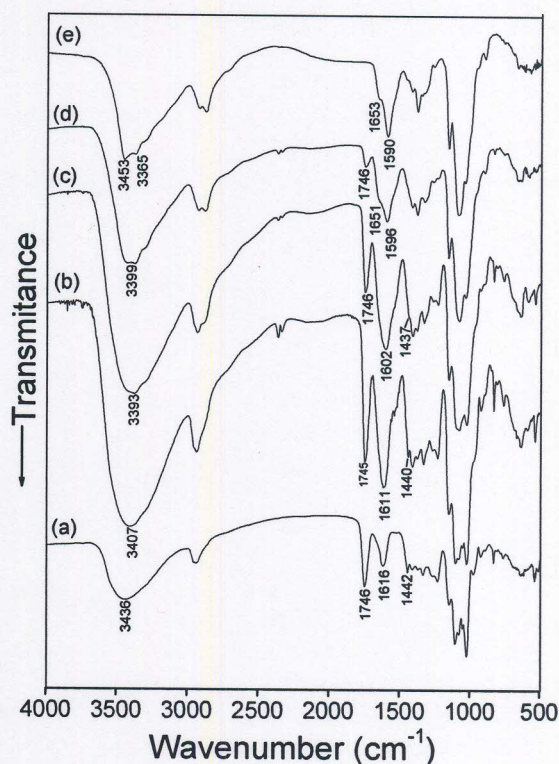


Figure 6: FT-IR spectra in transmittance mode of films for PEC (a), blends CHT/PEC 25/75 (b), 50/50 (c), 75/25 (d) and CHT (e)

The spectral region below  $1500 \text{ cm}^{-1}$  for both PEC and CHT comprehends the "fingerprint region" of biopolymers which contain high overlapping of skeletal C-O and C-C vibration bands of glycosidic bonds and pyranoid ring, making difficult the exact band assignment [14].

The FT-IR spectra of CHT/PEC blend films showed some modifications in typical bands when compared to the spectra of the PEC and CHT pure films. The intensity of  $\nu(\text{OH})$  band increased for blend films and it was shifted to lower wavenumbers reaching to  $3393 \text{ cm}^{-1}$  for blend 75/25. It is an indicative that the hydrogen bond system formed by hydroxyl groups, which stabilizes both CHT and PEC conformation in



solid films, becomes stronger by formation of blend. Spectra of the blends also changed in the carbonyl-amine region. The bands at 1653 and 1590  $\text{cm}^{-1}$  of CHT have combined with  $\nu_{\text{as}}(\text{C}=\text{O})_{\text{COO}}$  band of PEC forming a large single band, which is more evident in the spectra of blends 50/50 and 25/75. The  $\nu_{\text{as}}(\text{C}=\text{O})_{\text{COO}}$  and  $\nu_{\text{s}}(\text{C}=\text{O})_{\text{COO}}$  bands of PEC were shifted to lower wavenumbers reaching to 1602  $\text{cm}^{-1}$  and 1437  $\text{cm}^{-1}$ , respectively, for blend 50/50. Such modifications in the vibrational profile of FT-IR strongly indicates that the chemical environment of the groups of CHT and PEC has changed due to chemical interactions between them.

Differences in tensile strength also were observed among films, as shown in Figure 7. While CHT and PEC pure films showed tensile strength (TS) values at 41 and 48 MPa, respectively, the experimental date for CHT/PEC blends showed a positive deviation from the addition law.

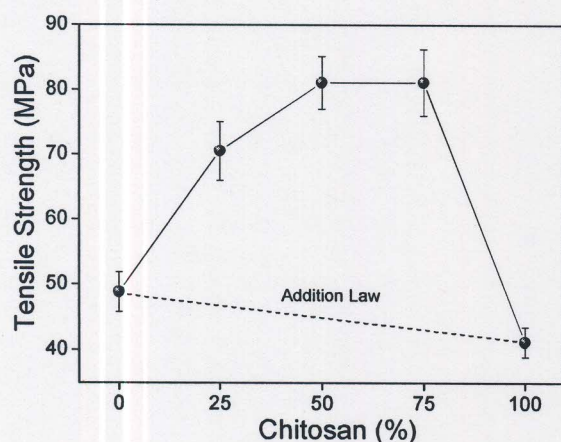


Figure 7: Tensile Strength (TS) values for pure polymer and blend films. Addition law is illustrated for comparison.

TS value for CHT/PEC blends were practically 100% higher than pure films. TS value for blend 75/25 was 70 MPa and reached to 81 MPa for blend compositions 50/50 and 25/75. The synergistic effect on TS for CHT/PEC blends demonstrates that strong interaction resulting from blending process provides high mechanical properties for blend matrix. Such results corroborate with vibrational characteristics found in FT-IR spectra of CHT/PEC blend films and are compatible with the formation of gel network shown in the results obtained from zeta potential and rheological characterization of blend solutions.

## Conclusions

Homogeneous blend films have been successfully produced from solutions of natural polymers chitosan and pectin. By controlling the ratio of chitosan and pectin, different behaviors were obtained in the solution state and resulted in better mechanical and water affinity properties for blend films. The chitosan/pectin blends developed in this work show

superior properties when compared with neat polymer films allowing to explore new applications of chitosan and pectin for biomedical, agricultural and food packaging devices.

## Acknowledgements

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