

## Cashew Gum-Chitosan Blended Films: Spectral, Mechanical and Surface Wetting Evaluations

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**Abstract:** Blends of cashew tree gum with chitosan and glycerol as plasticizer were prepared by casting and characterized by Fourier transform infrared spectroscopy (FTIR), mechanical (DMA) and thermogravimetric analysis (TG), scanning electron microscopy (SEM) and surface wettability by static contact angle measurements. FTIR analysis confirmed the consolidation of both polysaccharides and revealed a clearly interaction between the glycerol molecules and hydroxyl groups of chitosan. Chitosan and glycerol improved films mechanical properties and interferes on surface wettability. The unblended cashew gum films presented hydrophilic surfaces (medium measure angle as 40°) and with the addition of chitosan provides a shift towards a more hydrophobic behavior (52° and 75° for additions of 0.5% and 1.0% (w/w) chitosan respectively). Microscopy surface observation confirmed that the presence of glycerol reduced film cracking, changing them from fragile to a more plastic property. The film forming ability of chitosan is also preserved when blending with cashew gum.

**Keywords:** cashew-gum, chitosan, cast films, wettability, biopolymeric blends.

### Introduction

Thin films prepared from natural polymers have become strategically important in a variety of biotechnological applications including, among several possibilities, systems of drug carriers, active packaging for food conservation, membranes for wastewater treatments, biocompatible scaffolds, *etc.* Polysaccharides, from different sources, have been tested for such purposes and amongst them is the cashew-tree gum (CG), an abundant raw material suitable for chemical manipulation and film processing.

CG is synthesized in the epithelial cells in the bark of cashew tree (*Anacardium occidentale* L.) and secreted out as a defense response to trunk injuries. It is collected as a fragile, solid yellowish-brown resin with an appearance and texture similar to amber. CG is water soluble and can be transformed into a gel and then processed as flexible films by blending with other polymers and small additions of plasticizers.<sup>1,2</sup>

Structurally CG is a complex high molecular weight and branched heteropolysaccharide with an average chemical composition of galactose (72%), glucose (14%), arabinose (4.6%), rhamnose (3.2%), and glucuronic acid (4.5%).<sup>3</sup> The *Anacardium occidentale* L. tree however, requires a tropical climate to grow, resulting in gum characteristics that are very

seasonal and regional-dependent. This can affect gum density, color and final composition.<sup>4</sup>

Some studies reported that CG has antifungal<sup>5</sup> and antibacterial<sup>6</sup> properties against selected pathogenic and spoilage bacteria. Additionally CG has been evaluated for possible applications in medical-pharmaceutical fields, as adjuvant in drug formulations,<sup>7</sup> as scaffolds for cell growth,<sup>8</sup> as ionic coupling medium in electrochemical biosensors,<sup>9</sup> and as drug carrier matrix.<sup>10,11</sup>

Despite the good biocompatibility, one disadvantage in using cashew gum in raw state is its high hygroscopy that can result in fast water absorption. This makes it unsuited for applications as membrane or particles in delivery systems, due to elevated swelling rate quickly translating into matrix instability.

A blend of similar polymers offers an alternative that can partially overcome limitations due to water uptake instability and poor mechanical properties. Chitosan (Chit), a linear aminopolysaccharide derivative of chitin is such a candidate for blending. Chit has good film-forming characteristics and satisfactory chemical-resistant properties, having the ability of associating with a variety of polymeric structures.<sup>12-14</sup>

In the present study CG-Chit mixtures were prepared and cast into films. Structural, mechanical, thermal and hydrophilicity features were characterized devising possible applications in food packaging or medical devices.

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## Experimental

**Gels and Films Preparation.** Crude exudate gum was provided by Embrapa Agroindústria Tropical (CNPAT, Fortaleza, Brazil) and collected from cultivated *A. occidentale* L. trees. The gum was first ground for composition homogenization and purified according to procedure described by Costa *et al.*<sup>15</sup> The purification process comprised three repeated sequence of precipitation, filtration and drying. Initially the aqueous solution of crude gum (4% w/v) was neutralized with NaOH, filtered, precipitated in absolute ethanol, filtered again and dried at 50 °C until attaining constant weight. In a second step, the gum was dissolved in NaCl aqueous solution (5.0% w/v), filtered, precipitated in ethanol and dried at the same temperature. Finally the resulted gum was re-dissolved in distilled water, filtered and dried again. This sequence assures the elimination of most of impurities and insoluble debris in addition to replacement of cations in the gum, as K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup> by Na<sup>+</sup>.<sup>15</sup>

The chitosan (Chit) used was a medium molecular weight, purchased from Sigma-Aldrich, (Milwaukee, WI, USA). The gel was prepared by dissolution in two concentrations (0.5 and 1.5% w/w) in 1.0% acetic acid solution under constant stirring for 2 h at room temperature. The films formulations were prepared by mixing separately the Chit gels with purified CG which was previously dissolved in deionized water at a single concentration of 5.0% (w/w). Glycerol (1% w/w, from Synth, R. de Janeiro, Brazil) was also evaluated considering that this amount was successfully used as plasticizer for CG blends film processing.<sup>1,16,17</sup> The tested formulations are summarized in Table I.

Films were prepared by solution casting onto acrylic plates. Solvents were allowed to evaporate at room temperature. After drying the films were peeled off from the plates.

**Infrared Spectroscopy.** IR spectra were obtained using a Spectrum 100 spectrometer (Perkim Elmer, Nonvank, CT, USA) under dry air, at room temperature. The films were ground with powdered potassium bromide (KBr) and pressed into pallets. The spectra were the average of 50 scans recorded at a resolution of 4 cm<sup>-1</sup> in the range from 4000 to 450 cm<sup>-1</sup>.

**Mechanical Properties.** Film thickness was measured using a digital micrometer (Mitutoyo Corporation, Kawasaki-shi, Japan). Three values were taken at random locations along the length of three samples of each formulation and the mean value used for calculation. Dynamic Mechanical Analysis (DMA) was carried out using a TA Instrument DMA 2930, operating in fixed frequency and film tension mode. Film strips of dimensions 15.0 mm (height) and 6.0 mm (width) were cut for testing. Three samples were evaluated for each composition.

**Thermo-Gravimetric Analysis and Contact Angle Measurements.** TGA was used to evaluate the thermal stability and to determine the decomposition temperature of CG-Chit blends. Thermogravimetric measurements were performed using a TA Instruments model TGA Q500. Approximately

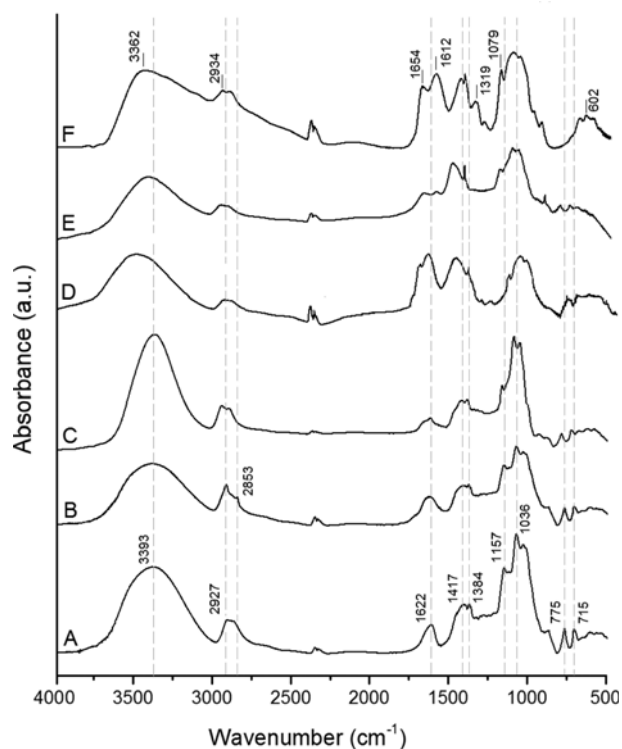
6 mg of each sample was weighed and sealed in platinum pans. The temperature range studied was 25-800 °C, at a heating rate of 10 °C per minute in nitrogen atmosphere. Mass changes were continuously recorded as a function of temperature.

The change on surface wettability due to the mixture content was estimated by contact angle measurements using the sessile deionized water drop method (around 5 µL). Contact angles were statically registered in a CAN101 Optical Contact Angle Meter (KSV Instruments - Finland). The recorded contact angle was the average of six measurements on each sample.

**SEM Observation.** Scanning electron microscopy of film surfaces was performed with a Jeol JSM-6510LV microscope. Strips of film were mounted on aluminum stubs and coated with gold using a Balzers Union Sputtering. All of the samples were examined under an accelerating voltage of 2.5 kV.

## Results and Discussion

**Spectroscopy Analysis.** In Figure 1 is shown the infrared spectroscopy in absorbance mode, resulting from the cast films. Neat CG and neat Chit film spectrum are marked with A and F letters respectively according to adopted identification as displayed in Table I. The spectra, particularly Chit have been widely interpreted in the literature,<sup>18-20</sup> and at large, both materials present vibrational patterns typically found in most of polysaccharides structures.<sup>21</sup>



**Figure 1.** Infrared spectra of neat CG and chitosan and their combination with glycerol according to identification as displayed in Table I.

**Table I. Gel Formulation Compositions for Film Processing**

Film	CG <sup>a</sup> (wt%)	Chit <sup>b</sup> (wt%)	Gly <sup>c</sup> (wt%)
A	5	0	0
B	5	0.5	
C	5	0.5	1
D	5	1.5	0
E	5	1.5	1
F	0	1.5	0

<sup>a</sup>Cashew gum. <sup>b</sup>Chitosan. <sup>c</sup>Glycerol.

Some common bands characteristic from these polymers are identified and possible to see that most of peaks are shifted towards longer wavenumbers in neat CG, when compared to neat Chit.

For neat CG film (Figure 1(A)), a large band centered at 3393 cm<sup>-1</sup> is assigned hydroxyl -OH and -NH groups stretching, occurring in all polysaccharide structures. The less intense absorption band located near 2927 cm<sup>-1</sup> may be attributed to symmetric and asymmetric C-H group stretching in the glucosamine ring, also a typical polysaccharide vibration. The band around 1622 cm<sup>-1</sup> is characteristic of C=O and C-C stretching frequency of glucuronic acid, confirming the presence of the -COO group. Subsequent bands around 1417 e 1384 cm<sup>-1</sup> are characteristic of -CH<sub>2</sub>-scissoring and the peaks of the shoulder at 1157 cm<sup>-1</sup> could be attributed to the COH stretching vibrations of CH<sub>2</sub>-O-CH<sub>2</sub> from glucosidic bonds and the O-H bending.<sup>20,22</sup> The intense peaks centered at 1036 cm<sup>-1</sup> indicates high amount of C-O groups,<sup>23</sup> characteristic of exudates polysaccharides as interpretation presented by Mothé *et al.*<sup>24</sup> Peaks at low wavenumber, as those at 775 and 715 cm<sup>-1</sup> are assigned as =C-H out-of-plan bending.<sup>23</sup>

The Chit spectrum (Film F) follows similar bands with some distinctions related to absorbance intensity and frequency of vibrations. The stretching of OH groups is enlarged with the main peak shifted to 3362 cm<sup>-1</sup>, probably overlapping the correspondent vibrations of N-H, and C-H bond in -CH<sub>2</sub> groups in the same region. It is observed the band split into two peaks around 2934 cm<sup>-1</sup>, resulted from the axial deformation of C-H from CH<sub>2</sub> and CH<sub>3</sub> groups from the glucosamine unit in the Chit structure, which is a single like peak and better defined in the CG spectrum. A clear doublet at 1654 cm<sup>-1</sup> (attributed to the C2 position in the NH<sub>2</sub> group of amino) and a typical signal at 1612 cm<sup>-1</sup> (which corresponds to the NH bending of amide II in vibrational mode) is observed, this last one close to correspondent acid stretching (-COO group) identified for the gum. A medium intensity vibration at 1319 cm<sup>-1</sup> is characteristic of -OH, -NH<sub>2</sub> or -CO groups and visualized only in Chit spectrum.<sup>18</sup> The vibrations 1079 cm<sup>-1</sup> is correspond to the group as identified at 1155 cm<sup>-1</sup> in the CG spectrum and associated to -C-O-C- stretching in glycosidic linkage.<sup>25</sup> A multiple peaks at short wavenumber as those centered at

602 cm<sup>-1</sup>, have been interpreted as the region of  $\alpha$  and  $\beta$ -anomers bending in glucose structure.<sup>26,27</sup>

Small addition of Chit (0.5% wt, Film B) did not perform significant changes in individual CG spectrum. Variations on absorbance intensities are noticeable in C-O correspondent band in 1036 cm<sup>-1</sup> region, probably due to amount of analyzed material. There is also a clear enlargement and unfolding of original band centered at 2927 cm<sup>-1</sup>, resulting in a double peak shape both correspondent to symmetric and asymmetric CH<sub>2</sub> group stretching typically related to chitosan glucosamine ring as commented before.

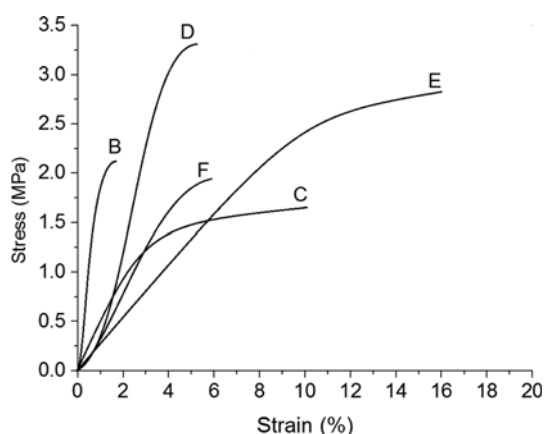
When blending with chitosan is 1.5% w/w (Film D), the multiples peak characteristics of amide I and II region stretching became more intense. There is an evident increasing on the absorbance bands at 1654-1612 cm<sup>-1</sup> due the presence of NH<sub>3</sub><sup>+</sup> of Chit and the CH<sub>2</sub>-scissoring at 1079 cm<sup>-1</sup> region appears as one defined band. These results suggest a blend consolidation by both polymers.

The incorporation of 1% w/w of glycerol as plasticizer (Films C and E) resulted in different effect depending on the Chit concentration (0.5 or 1.5% w/w) in the blend. In the spectrum of film C (low amount of Chit) there are few modifications related to A or B film spectra shape. All original bands of neat CG are preserved with a marked increase in the area under OH stretching vibration band, centered at 3393 cm<sup>-1</sup>. According to Cerqueira *et al.*,<sup>17</sup> such increasing is related to the glycerol hydrophilic nature and due to the hydrogen bonds formed by the hydroxyl groups in the galactomannan and glycerol structures. In film E, with 1.5% wt Chit, the presence of glycerol markedly reduces the typical chitosan bands associated to -NH groups of amide I and amide II bands between 1654 and 1319 cm<sup>-1</sup>. According to Ko *et al.*<sup>28</sup> these chitosan amide bands tend to disappeared when the acetamide groups are substituted by primary amine groups. Haq *et al.*<sup>29</sup> argument that the addition of small fractions of glycerol into a polysaccharide structure, bonds preferentially with polymer hydroxyl and polar groups, resulting in changes on peak intensity rather than on shift of the wavenumber.

These observations support that the formation of CG-Chit-Glycerol blended film is consolidate mainly by bonding taking place between the glucuronic acids in CG structures to the amino groups of chitosan linked by a net of hydrogen bonding formed between hydroxyl groups present in CG, Chit and glycerol.

**Mechanical Properties.** The films processed by the combination of CG and Chit exhibit a variety of mechanical properties which are strongly dependent on the polymers proportion and the addition of plasticizer as shown by Figure 2. Cast neat CG gum resulted in a discontinuous and extremely brittle film inadequate for mechanical analysis.

The stress x strain curves shows typical viscous behavior with a small modulus of plasticity with variable mechanical strength when assessed in terms of the tensile strength at break and percentage elongation (Table II). Chit has a known film



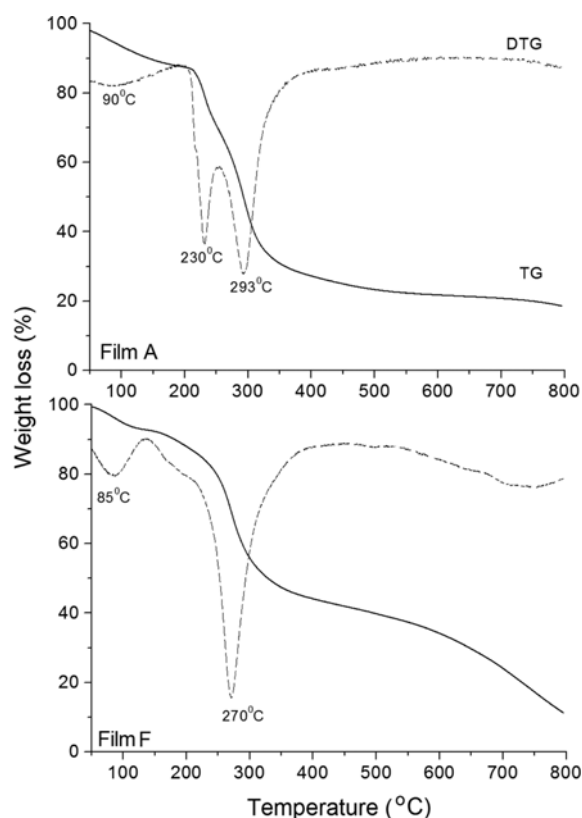
**Figure 2.** Tensile stress-strain curves for the CG-Chit cast films. The curve letters correspond to composition as presented in Table I.

**Table II. Values of Tensile Strength (MPa) and Maximum Strain (%) for Cast Films as Formulations Displayed in Table I**

Film	Strength at Break (MPa)	Maximum Strain (%)	Thickness ( $\mu\text{m}$ )
A	-	-	70.9
B	$2.12 \pm 0.58$	$1.61 \pm 0.54$	$63 \pm 1$
C	$1.66 \pm 0.41$	$9.99 \pm 1.06$	$66 \pm 7$
D	$3.31 \pm 0.94$	$5.29 \pm 1.98$	$66 \pm 2$
E	$2.76 \pm 1.01$	$16.03 \pm 3.26$	$58 \pm 6$
F	$1.92 \pm 0.29$	$5.96 \pm 0.83$	$54 \pm 7$

forming ability and when blend with CG resulted in an increasing in plasticity leading the elongation from  $1.61 \pm 0.54$  for addition of 0.5% (Film B) to  $5.29 \pm 1.98$  when 1.5 wt% of chitosan was mixed (Film D), with small, but positive effect on the tensile strength (from  $2.12 \pm 0.58$  to  $3.31 \pm 0.94$ ). The combination of 5.0% CG and 1.5% chitosan resulted in better properties than found to Chit film itself (Film F), indicating good interaction between materials. The addition of plasticizer in these formulations (Films C and E), despite reducing the strength at break, when compared to CG-Chit film (D), promotes the better plasticity with the highest extent of elongation. The effect of glycerol as plasticizer is well discussed in the literature.<sup>30</sup> Glycerol is a small molecule which easily forms hydrogen bonds with the polysaccharides polar functionalities. These interactions reduce the intermolecular forces along the chains increasing the internal free volume, facilitating chains mobility and consequently increasing the elongation. The reduction of intermolecular forces however, also reduces the resistance of the matrix to support loads reflecting in a lowering in the tensile strength.

**Thermal Characterization.** The thermogravimetric curves of neat CG and Chit films are presented in Figure 3. The solid curves (identified as TG) give the direct reading as obtained from the experimental procedure here adopted. The dashed



**Figure 3.** TG and DTG curves of cashew gum and chitosan, films A and F respectively (heating rate 10 °C/min).

DTG curves (mass derivative) allow the clear identification of each thermal event undergone by the sample. Both materials present the same pattern with continuous weight loss in one initial dehydration step, followed by additional decomposition events.

The neat CG TG curve (Film A) reveals three distinct decomposition stages. The first at 90 °C corresponds to desorption of physical and chemical bounded water. The second is evidenced at 230 °C and third more intense exothermic event is centered at 293 °C. Both are related to backbone degradation where the depolymerization, decarbonylation, pyrolytic decomposition and formation of water, CO, and CH<sub>4</sub> take place.<sup>31</sup>

Film F exhibits two typical thermal events largely characterized in Chit structure. The first one occurs between 37-135 °C, with a maximum at 85 °C corresponding to the removal of absorbed moisture and bounded water. Then, chains begin to degrade in the temperature interval between 210-370 °C, resulting in an intense exothermic event with a maximum at 270 °C. In the decomposition interval, complex processes can occur including the dehydration of the saccharide rings, depolymerization and the decomposition of acetylated and deacetylated units of Chit. The recorded thermal intervals are in good agreement with data presented in the literature.<sup>32-34</sup>

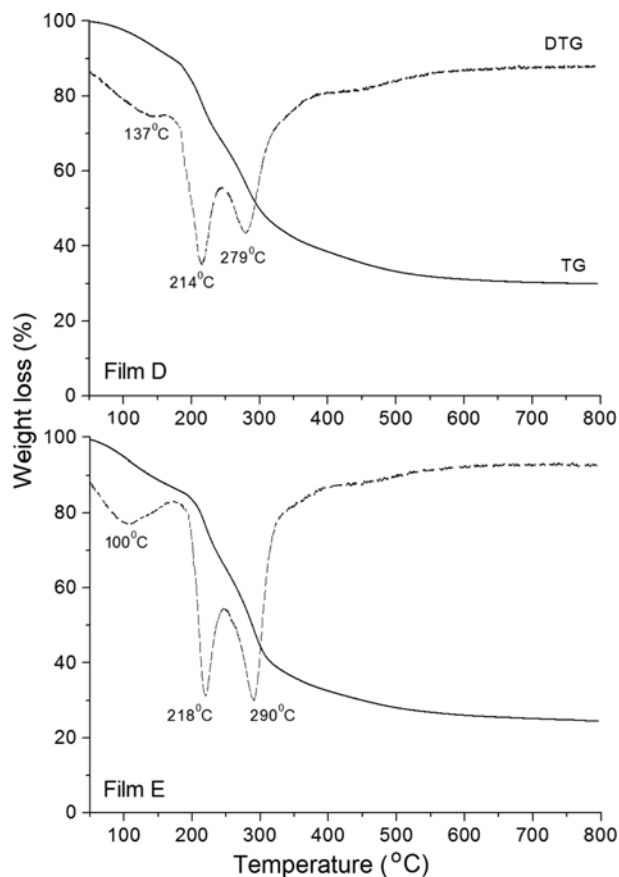
Compared to CG (Film A), despite an initial loss of water at lower temperature the TG curve describes a slower ther-

mal degradation for Chit film (F) what can be associated to the stronger intra-molecular bonding found in Chit structure. In other words, neat CG presents an inferior thermal stability when compared to neat Chit. The higher residual mass at 800 °C as found to CG is credit to large amount of remaining impurities present in exudate gums.<sup>19</sup>

For CG-Chit blended films the thermal behavior is close to that record for unblended CG, independent of the amount of Chit added. Table II summarizes the main thermal results. All blended films showed a dehydration process at a higher temperature than that registered for Chit film F, indicating a strong affinity to water, due probably to the higher density of polar sites presents in CG structure.

The degradation process also follows two steps (ranging from 214 to 293 °C) with a shift in initial decomposition to lower temperature, reflecting a reduction in thermal stability. An increasing in residual mass at 800 °C is also observed in blended films when compared to neat Chit film F.

The addition of a small amount of plasticizer to the blends results in few changes to their thermal behavior. By comparing the thermograms of same formulation with and without glycerol addition (1% w/w), films D and E respectively, the patterns are quite similar, with thermal occurrences in close temperatures (Figure 4 and Table III).



**Figure 4.** TG and DTG curves of CG-Chi blended films; without and with plasticizer (glycerol at 1% w/w concentration).

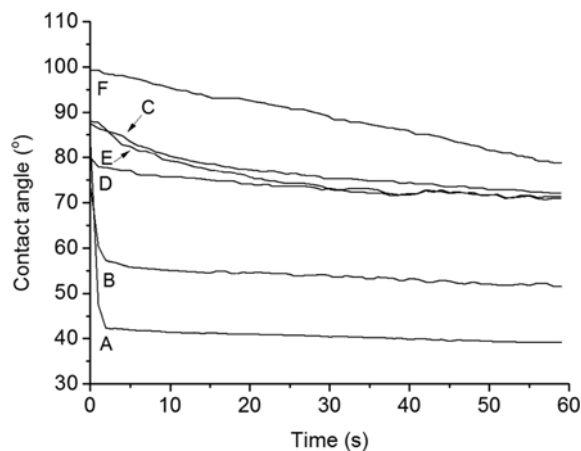
**Table III.** Thermal Parameters from TGA Curves

Film	Dehydration Temperature (°C)	Maximum Decomposition Temperature (°C)		Residual Mass at 800 °C
		$T_{d_1}$	$T_{d_2}$	
A	90	230	293	19.6
B	87	236	291	25.0
C	120	221	292	17.7
D	135	214	279	30.0
E	100	218	290	24.5
F	85	270	--	11.3

The main difference observed is an increase in the temperature interval between the decomposition events. Film E presents the wider gap (72 °C) indicating a reduction on degradation kinetics. This is in agreement with analysis performed by Cardenas and Miranda,<sup>35</sup> who reported an increase in polymeric structural stability when small amount of plasticizer was added to Chit based films. This result indicates a strong intermolecular interaction between the glycerol molecules and the polysaccharides chains, confirming the spectroscopy analysis.

**Wetting and SEM Analysis.** Regarding the hydrophilicity, the recorded water contact angles on films surfaces are shown in Figure 5. Two distinct hysteresis behavior on films A and F are observed. Chit (Film F) has an initial hydrophobic angle (around 100°) with a typical time-dependence behavior with receding hysteresis pointing to a gradual increase in wettability, with a tendency to stabilize afterwards (around 85-80°). Such a profile is typical and in good agreement with values found in the literature for Chit based films.<sup>36,37</sup>

The receding behavior observed in Chit film could be interpreted as indicative of multiples mechanisms acting simultaneously as water sorption, liquid spreading, trapping and



**Figure 5.** Water contact angles variation with time as measured on films surfaces. The identification letter corresponds to gel precursor solution as displayed in Table I.

swelling due to the capillary effects. These reflect the reorientation of the hydrophilic moieties towards the surface when contacting water drops.<sup>38</sup> All these mechanisms are common to most biopolymers and the predominance of one or another is dependent on the surface's chemical properties.<sup>39</sup>

Contrastingly the neat CG film (A) has an initial contact angle close to 84° but it decay immediately after drop deposition stabilizing in approximately 40°. Such value characterizes a hydrophilic material and the immediate reduction of the angle can be interpreted as the spontaneous penetration of the water inside the matrix *via* percolation (absorption) consistent with hydrophilic polysaccharide wetting model as proposed by Farris *et al.*<sup>39</sup>

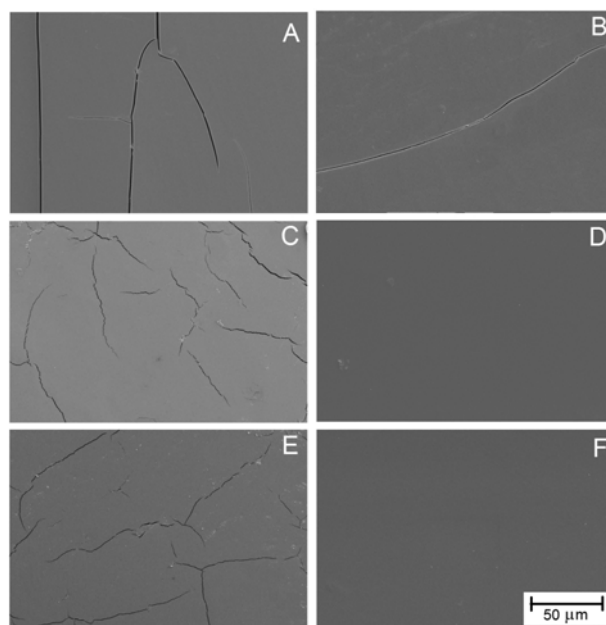
By comparing only films A and F it is evident that the Chit is considerably more hydrophobic than CG. As the chitosan content in the blend increases (Films B and D) the surface tends to behave more hydrophobic with contact angle stabilizing at 52° for film B and around 75° on film D. It is worth noting that the addition of just 0.5% w/w Chit (Film B), significantly reduces the angle hysteresis. That is a consequence of CG-Chit polar groups' interactions, mainly through hydroxyl functionalities, reducing its availability for external water bonding.

Of particular interest is the result concerning the addition of 1% wt glycerol as plasticizer (Films C and E), showing that independent of the Chit proportion the plasticizer introduces identical behavior: an initial angle of approximately 87° with a smooth decay stabilizing around 75-78°. Glycerol molecules (C<sub>2</sub>H<sub>8</sub>O<sub>3</sub>) have one hydrogen group on each carbon, which confers a high polarity and facility to bind preferentially to polysaccharide's hydroxyl groups,<sup>35</sup> also affecting surface water interactions. In sum, the combination of CG-Chit with small addition of glycerol, allows the processing of flexible films with inferior hydrophilicity than that measured to neat gum.

General SEM observations of the different films allow the identification of the effect of Chit and glycerol additions. As seen in Figure 6 the cast film from neat CG (Film A) forms a regular smoothed surface, though with cracks propagating along the matrix. This film is brittle and difficult to be handled. The fractures alignments and the formation of crack-bridging evidence a fragile matrix behavior.<sup>40</sup>

The addition of 0.5% w/w Chit (Film B) confers a reduction in the cracking density, nevertheless without eliminating it completely. Some long cracks can be observed on the surface still in a fragile pattern.

When 1% wt glycerol is added to the formulation (Film C) the cracks are still present in the structure, though they appear different. For plasticized films the cracks are not continuous or propagated in a straight pattern. They are irregularly distributed in the matrix and with curved and interrupted fractures, revealing a tendency to a ductile behavior. No signs of phase separation between the components are identifiable, indicating that the polymers and the plasticizer are physically



**Figure 6.** SEM micrographs of casting films. The identification letters correspond to compositions as showed in Table I.

compatible with each other. These characteristics are also observed to film E. Despite the observed surface discontinuities, both films (C and E) are fully manageable.

The most smooth and homogeneous films were attained when chitosan addition was 1.5% w/w, without plasticizer (Films D and F). A very regular flat surface was formed in both formulations with no cracks or visible imperfections, confirming the Chit ability in forming continuous films.

## Conclusions

Homogeneous films can be obtained by casting from adequately adjusted solution of cashew gum and chitosan. Infrared spectral analysis shows that small amount of chitosan (0.5% w/w) did not change the gum structure significantly. When blending with chitosan is 1.5% w/w the multiples peaks characteristics of amide I and II region became more intense and the stretching vibration of CH<sub>2</sub> group appears as one defined band, suggesting consolidation of both polymers. With the addition of glycerol as plasticizer, interactions were registered mainly with hydroxyl and amino groups in chitosan matrix. The blending of cashew-gum with chitosan did not change significantly the gum thermal behavior. Conversely, the blending with chitosan and the addition of 1% w/w of glycerol heavily interferes with mechanical and wetting properties. The combination of 5% gum with 1.5% chitosan and 1% glycerol promotes the best mechanical behavior and also changes the surface towards a more hydrophobic behavior. These are important results to consider when devising applications for these films. All formulations, with the exception of neat cashew gum film

(extremely fragile), are quite manageable, allowing handling. The chitosan ability of forming films was confirmed as well as the feasibility of using the combination cashew-gum/chitosan in preparing polymeric blends.

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