

# Bionanocomposites Based on Pectins and Halloysite Nanotubes

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## INTRODUCTION

During the past century, there has been a lot production of plastic materials which contributed significantly to improve the quality of human life due to their remarkable versatility in various applications. These materials are practically un-degradable generating serious environmental risks. One of the urgent problem arises from the products widely employed in packaging. Therefore, some efforts have been addressed at reducing the packaging waste by exploiting a new class of bio-degradable materials. It is worth-noting that such bio-materials can also offer economic advantages because they are derived from renewable resources.<sup>1,2</sup> Apart from the packaging area, the potential applications of bio-materials are numerous and involve different fields such fibers for the textile industry, medical products, engineering applications, and so on. A recent review<sup>2</sup> reported that several biopolymeric materials (collagen, gelatin, chitosan, chitin, cellulose, starch, pectin, etc.) have been used to make films and formulations. Films based on pectin and additives (such as polyvinyl alcohol, chitosan, etc.) can be potentially used as water-soluble pouches for detergents, softeners and medical delivery.<sup>2</sup> Pectin blended with high amylase starch and glycerol form edible films with a large interval of mechanical properties<sup>3</sup> and excellent oxygen barrier capability.<sup>4</sup> Moreover, pectin-protein composite films may be used in wrapping and packaging materials in cases where moderate mechanical strength and low water vapour transmission are required.<sup>5</sup> These materials would be limited in their use because of dominant hydrophilic character, fast degradation and, in some cases, unsatisfactory mechanical properties<sup>6</sup>. Indeed, the thermal, mechanical, etc. properties of these materials can be improved by using inorganic fillers as additives. To our knowledge, only a few studies are available. Composites based on montmorillonite and biopolymers like pectin,<sup>7</sup> gelatin,<sup>8</sup> chitosan<sup>9</sup> and cellulose<sup>10</sup> were studied. The intercalated biopolymer chitosan in Na<sup>+</sup>-montmorillonite generated resistant three-dimensional composites with interesting functional properties.<sup>11</sup> Multiwalled carbon nanotubes improved the mechanical properties of chitosan.<sup>12</sup> We thought to shed some lights to this issue by preparing and characterizing new green composites formed by biocompatible components from renewable resources and environmental friendly. We selected two pectins with different degrees of esterification as biopolymer and halloysite nanotube as a green<sup>13</sup> filler which being natural products do not add any risk to the environment. We prepared the composites using the casting process. This work contributes to the improvement of the knowledge on green nanocomposites which might represent an alternative to the clay nanocomposites based on polymers derived from fossils.

## EXPERIMENTAL

**Materials.** Apple pectin (degree of methyl esterification, 74%, Mw=30-100 kg mol<sup>-1</sup>) and citrus pectin (degree of methyl esterification, 24%, Mw=30-100 kg mol<sup>-1</sup>) and halloysite nanotubes (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>·2H<sub>2</sub>O, HNTs) are from Aldrich. All the materials were used without further purification. For the dispersion preparation, we used water from reverse osmosis (Elga model Option 3) with a specific resistivity greater than 1 MΩ cm.

**Preparation of composites.** An appropriate amount of nanofiller (HNT) was added to the 2 wt % pectin solution prepared in water under stirring at 70 °C. The well dispersed aqueous mixture was poured into Petri dishes and heated at 80 °C for approximately 15 hours to evaporate water. The films (with a thickness of ca. 0.06 mm) were easily removed from the supports and stored in a desiccator at room

temperature. The composition of nanofillers (C<sub>f</sub>) expressed as weight percent (grams of filler/100 grams of nanocomposite) was systematically varied.

**Scanning Electron Microscopy.** The morphology of nanocomposites was studied using a microscope ESEM FEI QUANTA 200F. Before each experiment, the surface of the sample was coated with gold in argon by means of an Edwards Sputter Coater S150A to avoid charging under electron beam. Minimal electron dose condition was set to avoid damage of the sample.

**Films transparency.** The experiments were carried out at 25.0 ± 0.1 °C by using a Beckman spectrophotometer (model DU-640). The attenuation coefficient at the wavelength of 750 nm (K<sub>750</sub>) for each sample was computed as  $K_{750} = A/(2.3 \times D)$ , where A is the absorbance and D is the thickness of the rectangular film measured with a micrometer (±10<sup>-3</sup> mm). It has to be noted that at 750 nm both HNT and pectin do not show any adsorption band. K<sub>750</sub> of nanocomposites with C<sub>f</sub> > 30 wt % was not measured due to low transparency.

## RESULTS AND DISCUSSION

The prepared composites showed interesting features from the macroscopic point of view. The biocomposites exhibit compact mechanical features even for very high loading, and only for C<sub>f</sub> > 80 wt % the material appears fragile. This is not a general finding related to the pectin/clay composites to the light of our recent results<sup>14</sup> on pectin/laponite mixtures, which present a macroscopic structural deterioration at C<sub>f</sub> = 20 wt %. The degree of methyl esterification does not play a role.

The morphology of nanocomposites and therefore the distribution of the nanotubes into the polymer matrix was investigated by scanning electron microscopy (SEM). From the SEM micrographs, the structure of hollow tube with a spiral shape of HNTs is evident (Figure 1). A statistical analysis gave the average values of 73 ± 2 and 770 ± 20 nm for the radius and the length of the nanotube, respectively.

The micrographs of the HM pectin/HNTs and the LM pectin/HNTs systems show that the nanofiller is well dispersed into the polymer matrix and presents agglomerations only at very high filler compositions. In principle, HNTs provide two sites of interaction with pectin, i.e. the external surface and the inner cavity. The forces between the nanotubes compete with the interactions between nanotube and pectin which trigger the HNT-clusters formation. This phenomenon is retarded in LM pectin (C<sub>f</sub>>30 wt %) likely due to the larger amount of carboxylic groups in the polymer chain, which enhance interactions between the HNT outer surface and the pectin rendering the system more uniform. The film transparency data may give some light to this aspect. The efficiency of the light scattering from the film is certainly influenced by the morphology of the filler, the tendency to form aggregates and the filler concentration.

Computation of k values based on the size and the concentration of anisotropic particles and polydispersity is rather complicated. For spherical particles it is reported<sup>15</sup> that  $K_{750} \propto \phi R$  where R is the radius of the spherical particles scattering light while  $\phi$  is their volume fraction. Accordingly, the slope of the K<sub>750</sub> vs  $\phi$  trend is proportional to R. For our systems, R assumes a more general meaning that is an apparent radius of spherical particles having the same scattering property of the real particles. In the case of HM pectin/HNTs system (Figure 2), the linear trend of K<sub>750</sub> vs  $\phi$  in the domain to  $\phi = 0.10$ , (C<sub>f</sub> = 20 wt %) indicates that the individual particles did not form aggregates because a single R value is expected in that concentration regime. The deviation from linearity occurring at higher concentrations reflects the nanotubes organization into clusters with apparent radii increasing upon the filler addition. By replacing HM pectin with LM pectin (Figure 2), one observes a linearity in the entire range investigated (0 ≤ C<sub>f</sub> ≤ 30 wt %) reflecting the uniform dispersion of nanotubes. These results confirm the morphologies evidenced by SEM experiments and, once again, they highlight the role of esterification degree.

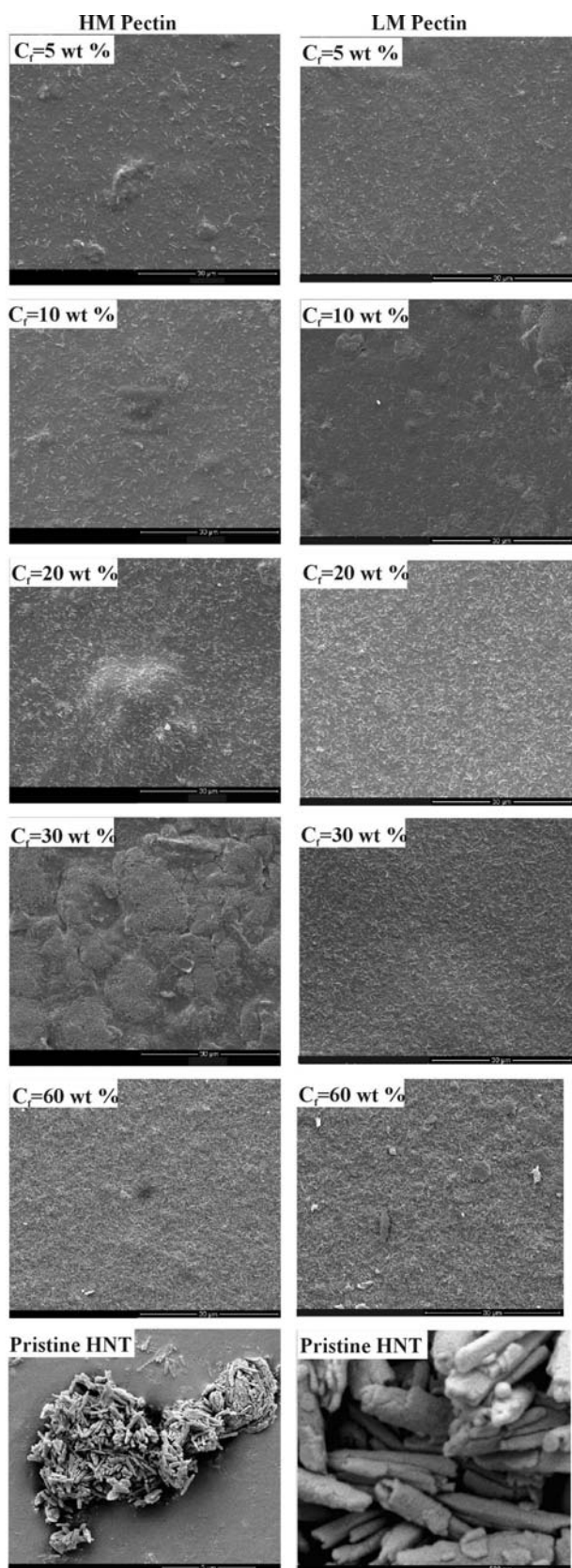


Figure 1. SEM images for nanocomposites based on pectin and HNT

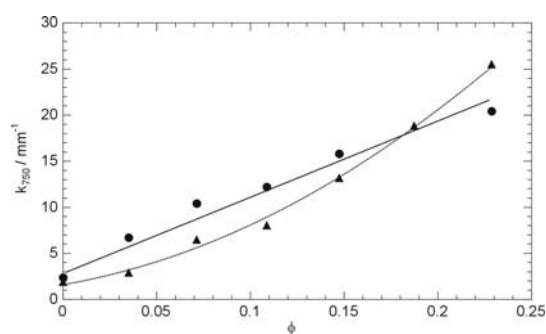


Figure 2. Dependence of  $k_{750}$  on the filler volume fraction for HM ( $\blacktriangle$ ) and LM ( $\bullet$ ) pectin mixed with HNTs.

The behavior of HNTs dispersed into the pectin matrix may be predicted through the percolation theory.<sup>16</sup> In general, a system of independent nanoparticles of cylindrical shape dispersed in a continuous medium upon increasing the volume fraction generates a system controlled by nanoparticle-nanoparticle interactions. Such a transition takes place at the critical value  $\phi_c$ , which based on that theory and from the radius and the length of the cylinder provided by SEM, corresponds to the  $C_f$  range between 11 and 21 wt %.

By further increase  $\phi$  the nanoparticles are completely interconnected and the system becomes rigid at a  $\phi_r$  value. For weakly interacting nanoparticles<sup>16</sup>  $\phi_r = 4\phi_c$  and therefore we obtained  $41 \text{ wt \%} \leq C_f \leq 70 \text{ wt \%}$  in agreement with the experimental SEM and transparency data.

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