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ORIGINAL ARTICLE

Reinforcement of poly (vinyl alcohol) films with alpha-chitin nanowhiskers

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Abstract

Composites Films were produced using Poly (Vinyl Alcohol) as the soft material and reinforced with Chitin Nanowhiskers(NWCH) as the rigid material. The present work studies the reinforcing mechanisms of NWCH in PVA films, made through a solvent casting technique and characterized for their calorimetric, swelling and mechanical properties. DSC tests revealed a sharp increase of 45 °C in glass transition temperatures with only 1.5% NWCH, while melting temperature had a small increases suggesting an anti-plasticizing effect. Swelling tests revealed decreasing hygoscopy when NWCH volume fraction increases. Estimates for elastic tensile modulus using a model that predicts the formation of a percolating network were not consistent with the experimental data of tensile tests suggesting that contrary to the reinforcement with cellulose nanowhiskers the percolating network is not primarily responsible for the reinforcement of the films. By adjusting the Halpin-Tsai equations, modified by Nielsen it was found that the mechanical properties were mainly influenced by the packing of the NWCH.

Keywords: *Chitin, Nanocomposites, PVA, Nanowhiskers, Reinforcement.*

1. Introduction

The dependence of non-biodegradable petroleum derived polymers such as polyethylene, polypropylene, terephtahlate (PET), poly styrene, etc can cause serious threats to the environment if alternatives aren't researched. Biodegradable polymers often show low chemical and physical properties when compared to the their counterpart[1,2]. One example of such polymers is Poly (Vinyl alcohol), PVA, which is a semi-crystalline thermoplastic produced from the deacetylation reaction of poly(vinyl acetate) and composed of large number of hydroxyl groups making it an hydrophilic polymer and totally soluble in water. It can be easily processed into thin films, and provides a good chemical resistance[3]. However, these properties occur only in the dry state, since this polymer is very hydrophilic and the water absorption decreases considerably their properties, even to dissolve it again. This feature substantially limits its field of application, requiring crosslinking usually with toxic chemicals[4].

Chitin is the second most abundant polysaccharide in nature, followed by cellulose, and its main source of commercial extraction are the shells of crustaceans[5]. This feedstock is an underutilized abundant solid waste from food industry, with a negative environmental impact that stems largely from shrimp processing industry using aquaculture as the main provider[6]. Novel materials from these sources are being considered eco-friendly due their biodegradability and because their use lessens or avoids petrochemical derivatives. It is considered that natural additives such as chitin nanowhiskers represents a major investment for environment preservation, being also interesting in industrial terms, if a composite have better behavior in water uptake or mechanical properties than the polymer itself[7]. The inclusion of nanowhiskers in different polymer matrixes, both synthetic and natural, proved to be advantageous in the strengthening of mechanical properties, water absorption and thermal stability. The mechanical properties enhancement is due to the interface created between polymer and nanowhiskers and interactions between nanowhiskers themselves[8]. Several studies with similar results performed for different systems, explain that for a specific amount of nanowhiskers, a percolation phenomena occurs leading to extensive hydrogen bonding between nanowhiskers thus increasing the composite mechanical properties[9-14]. The term percolation was first introduced by Hammersley in 1957[15], and refers to a statistical geometric model. This model can be applied to any system where it is expected to have a possibility of connection between constituents. Studies about cellulosic nanowhiskers have proven that the material reaches the percolation above a critical volume fraction[16]. This percolation threshold is the difference between the connection of a finite number of elements and a connection to an infinite number of elements[17]. The factors influencing this limit, are the aspect ratio of nanowhiskers, the possibility of occurrence of interactions between particles and their orientation. When applied to cellulosic nanowhiskers, this model allows describing the unusual increase on mechanical properties, since presupposes the formation of a rigid network between nanowhiskers. Presentlty it is still unclear weither this model is also valid for chitin nanowhiskers. Sriupayo and colleagues mechanically reinforced PVA films with chitin nanowhiskers but the mechanism of such reinforcement was not clarified[18]. In another work Roohani et al, reinforced PVA films with cellulose nanowhiskers but the percolation

model did not successfully fitted the experimental data[19]. Uddin and co-workers introduced highly oriented chitin nanowhiskers into PVA films resulting in a high increase of mechanical properties but when applying a rule of mixtures could not explained the reinforcement mechanism[20]. A recent work from Sonker et al, introduced cellulose nanowhiskers into crosslinked PVA films discovering a synergistic effect between the crosslinks and the nanowhiskers in tensile studies due to decreased chain mobility[21].

PVA / nanowhiskers composites are biodegradable and environmentally friendly materials which means its utilization is more beneficial to the environment than the use of non-degradable plastics[22]. Several works proved that the composites produced by inclusion of nanowhiskers elements in PVA may be useful for many applications in different sectors like food packaging, agriculture, chemical engineering and in medical field.that require some sort of barrier. Packaging materials require good barrier and mechanical properites which can be introduced by the nanowhiskers[23]. Mulching methodology in agriculture can also benefit from plastics with increased barrier properties and the films biodegradability[24,25]. PVA / nanocellulose hydrogels can be used as super-absorbents to deal with water pollution problems due to oils spills or chemical spilage[26]. In the medical field, PVA films could be used as wound dressings[10,27] and be doped with silver nanocrystals to increase bacterial resistance while protecting skin wounds[28] In all these cases, features such as chemical and mechanical resistance are decisive for the behavior of separation membranes.

The aim of the present work is to study PVA films reinforced with nanowhsykers of chitin, improving the calorimetric and mechanical properties PVA films. Additionaly, while for cellulose nanowhiskers its clear that the mechanical reinfocerment is trough a percolation mechanism, the mechanism behind the reinforcement with chitin nanowhiskers is not yet understood, so the intent of the present work is to clarify such mechanism using two different models.

2. Materials and Methods

2.1 Production of chitin nanowhiskers (NWCH)

Pandalus borealis shrimp shells were obtained from Aquamaris, João Pessoa, Brazil. Purified chitin was extracted adapting a previous reported procedure[29]. Briefly, frozen shrimp shells were firstly dried and grounded. Desmineralization step was performed using 1M aqueous solution of hydrochloric acid (Sigma-Aldrich, Reagent Grade), at room temperature for 1h then filtered and washed until neutral pH. Deproteinization was performed using 1M aqueous solution of Sodium Hydroxyde (Sigma-Aldrich, reagent grade) at 80 °C for 1h then filtered and washed until neutral pH. hydrolyzed with 3N hydrochloric acid for 1.5h at boiling temperature. The suspensions were then diluted with distilled water until pH was superior to 2. Above this pH the supernatant was stored for dialysis against water for complete neutralization. The neutralized suspensions were then freeze-dried, and dried chitin nanowhiskers were obtained.

2.2 Preparation of nanocomposite films

2.0 wt% PVA (ACROS, 95% hydrolysed, Mw = 95000) aqueous solutions were prepared by dissolving in water at boiling temperature for 1h and then stored overnight. Nanocomposite films were produced using different amounts of dried chitin nanowhiskers mixed with PVA solution, and subjected to 1 minute of sonication for complete homogeneization. The prepared solutions with 0, 1.5, 3.0, 5.6 and 10.0% of volume fraction (vf) of NWCH were cast with the aid of a calibrated ruler on a Teflon surface, and left to dry at laboratory atmosphere.

2.3 Characterization

Transmission electron microscopy (TEM) observations were made with a Hitachi H8100 electron microscope with an accelerating voltage of 100kV. A droplet of a dilute suspension (0.02 wt%) of chitin nanowhiskers was deposited onto carbon-coated grid and allowed to dry. No stain agent was used.

Infrared Spectroscopy (FTIR) Measurements were performed using a Spectrum 400, FT-IR/ FT-NIR Spectrometer Perkin Elmer. KBr discs were made by mixing 1mg of dried NWCH with 100mg of KBr.

Differential scanning calorimetry (DSC) was performed using a NETZSCH DSC 204F1 Phoenix. Each sample was heated from 25 to 250 °C at a heating rate of 10 °C/min. The melting temperature (Tm) was taken as the peak temperature of endotherm curve while the glass transition temperature (Tg) was taken as the inflection point of the specific heat increment at the glass-rubber transition. To determine the swelling index, PVA films with increasing NWCH concentrations were cut into 2.0 cm × 2.0 cm pieces and immersed in distilled water for small time intervals were swollen samples were taken out and wiped for excess water and then weighed. Tensile tests were performed using a Rheometric Scientific Minimat Firmware 3.1, at room temperature (22 °C). 15 samples of 5 × 2 mm were uniaxialy pulled at a speed of 5mm/min. From the stress-strain curves, the experimental elastic tensile modulus (Ec), the tensile strength (σ_u) and the elongation at break (ε_u) were determined.

3. Results and Discussions

Transmission electron micrographs obtained from a dilute suspension of chitin nanowhiskers. are presented in Figure 1a The suspension contains individual chitin fragments composed of slender parallelepiped rods that have a broad length distribution. These fragments have a length ranging from 50 nm up to 500 nm, and a width from 5nm up to 30nm. Nanowhiskers lengths are presentd using cumulative frequency curve at Figure 1b. The dimensions of the nanowhiskers were averaged from the analysis of 5 micrographs and more than 100 rods were analysed. The average length was found to be 303 nm and the average width 19.9nm. The average aspect ratio (L/d, L being the length and d the diameter) of these nanowhiskers is 15.9. Dimensions are similar to other previously reported works for chitin nanowhiskers from shrimp shells with lengths ranging from 150 to 500nm and widths close to 20 nm[30].

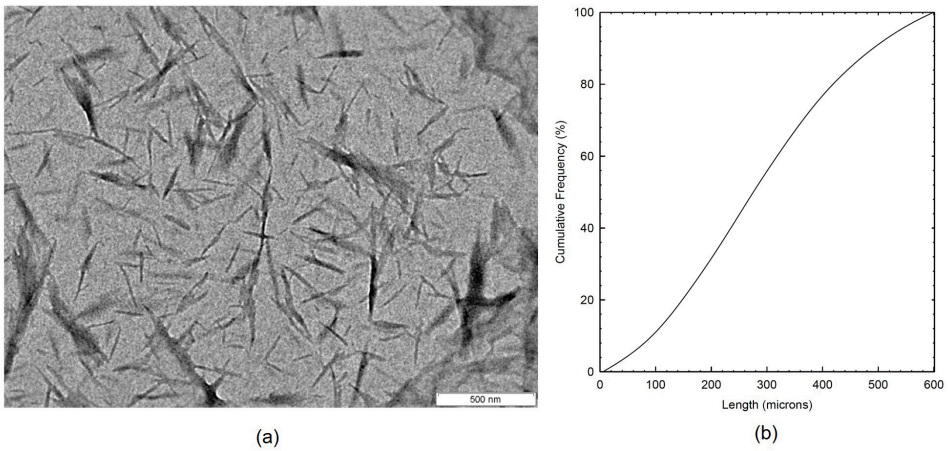

Figure 1. (a) TEM image of alpha-chitin nanowhiskers; (b) Histogram summarizing the determined lengths.

Table 1. Summary of DSC analized results for the nanocomposites.

Nanowhiskers Volume Fraction (%)	Tg (°C)	Tm (°C)
0	74	199
1.5	119	208
3.0	122	210
5.6	138	>250
10	-	>250

The infrared spectrogram in Figure 2 shows the presence of three typical peaks of alpha-chitin, observed for wave numbers 1658, 1622 and 1556 cm^{-1} corresponding to absorption of carbonyl group. The purity of the nanowhiskers can also be proven by the absence of proteins as indicated by the absence of absorption around the peak at 1540 cm^{-1}[31]. The deacetylation degree values, determined by the method elaborated by Brugnerotto et al., are very low, around 17% (significantly below 50%)[32].

The glass transition temperature (Tg) is a measure of the energy needed to allow movement of the polymeric chains on the amorphous domains. At this temperature the polymer becomes softer and when a force is applied, amorphous chains easily slip between each other. In Figure 3 it is presented the thermograms for all samples, with Tg being determined at the point of inflection of the first change in the slope and the melting temperature (Tm) at the endothermic peak.

Calorimetric characterization presented significant changes in the glass transition temperature, while for melting temperature (Tm), small increases were detected, as described in Table 1. The glass transition temperature of films with pure PVA is 74.7 °C and with only 1.5vf% NWCH, the value rose to 119 °C, corresponding to an increase of 45 °C. With increasing NWCH content, the differences in Tg are smaller and occur in a range of 20 °C. Given these results, it is considered that the NWCH have an anti-plasticizer effect within the PVA. The reason for this behaviour is related with the increased movement restriction of PVA chains adsorbed at nanowhiskers surface due to the establishment of hydrogen bonds between hydroxyl and acetyl groups from chitin with

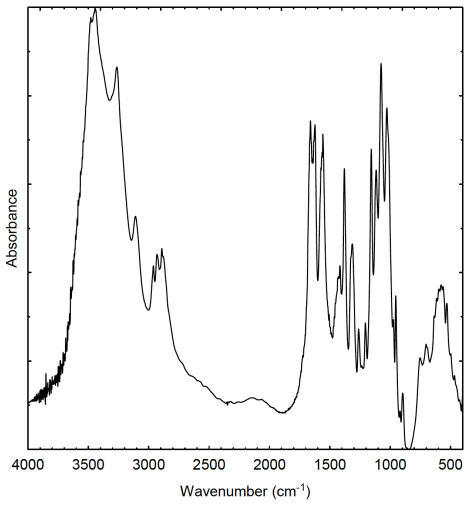

Figure 2. Infrared Spectrum of the chitin nanowhiskers.

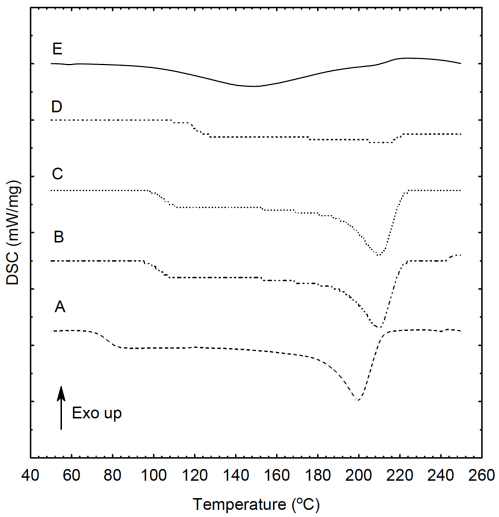

Figure 3. Thermograms for the nanocomposites(exo up): A = 0%vf; B = 1.5%vf ; C = 3.0%vf; D = 5.6%vf; E = 10.0%vf.

hydroxyl groups from PVA, Roohani et al also reported an increase on Tg for highly hydrolyzed PVA samples when reinforced with cellulosic nanowhiskers[19].

With regard to Tm, a slight increase of the melting temperature was detected and a possible explanation may be related to strong interactions between the chitin nanowhiskers and PVA chains resulting in higher number of crystalline domains on the matrix thus requiring more energy to be become free. This explanation is supported by the high degree of PVA hydrolysis. Similar results were obtained by Roohani et al., while testing PVA with different degrees of hydrolysis and cellulosic nanowhiskers[20]. For 5.6 and 10%vf samples, the material degrades, and it is not possible to detect a melting temperature for both composites. The anti-plasticizer effect is not a disadvantage in terms of film production methodology, since the only method used for production was by solvent evaporation, which is considered a slow but productive method that enables the formation of the aforementioned network of interactions between chitin-chitin.

As mentioned before, PVA films lack chemical and mechanical properties while wet, so to understand if the inclusion of NWCH could be beneficial to lessen the hygroscopicity, the swelling index was determined using Equation 1 for pure and reinforced samples.

$$Swelling(\%) = \frac{W_S - W_D}{W_D} \times 100 \quad (1)$$

The swelling behavior of pure PVA and reinforced films is ploted as a function of the submersed time at Figure 4. For every sample, the degree of swelling increased sharply for the first 5-10min of submersion, after which had a gradual increase until it reached an equilibrium weight at approximately 40min. Pure PVA films had the highest swelling index with 417%, followed 1.5%vf NWCH with 378%, while 5.6%vf NWCH samples had the lowest sweeling value of 119%. These results are in agreement with similar works, where the equilibrium swelling values were between 350% and 540%[18]. Nair and co-workers, also reported that chitin nanowhiskers reduce the ability of a rubber based nanocomposite to swell in the presence of Toluene[33]. Two factors should be considered while analyzing the swelling behavior of PVA films: one is the large number of hydroxyl groups that attract water molecules and the other is the PVA chains mobility. One combined with the other causes absorbed water to displace PVA chain resulting in increasing of dimensions and swelling. Eventhough chitin nanowhiskers have a large number of hydroxyl groups and thus attract more water molecules, this is overcomed by the reduction of the PVA chains mobility explaining the reduction of the swelling index.

Mechanical properties were assessed using tensile tests on small samples of nancomposite films. The obtained elongation at break and tensile strength for each volume fraction are displayed at Figure 4 and summarized at Table 2.

Analysing Figure 5, the results present an increase in the tensile strength required to break apart the nanocomposite film, and a decrease in the elongation sustained by the film, resulting in a composite with lower elasticity. A possible explanation for such result might be related with the presence

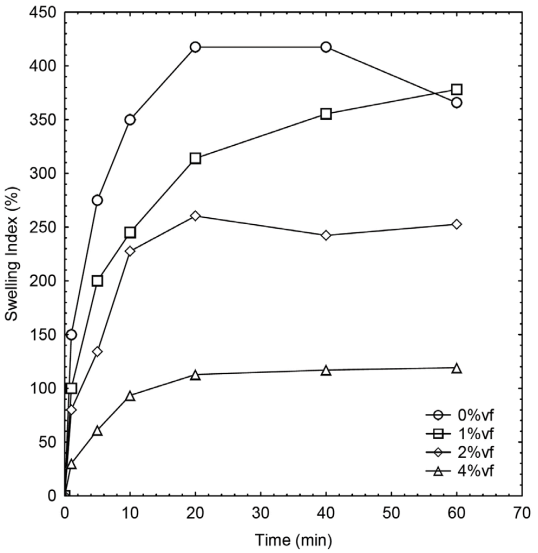

Figure 4. Swelling index for pure and reinforced samples: □ pure PVA; Δ 1.5%vf; ○ 3.0%vf; ◇ 5.6%vf.

Table 2. Summary of the composite films mechanical properties.

NWCH Volume Fraction (%)	Tensile Strength (MPa)	Elongation at Break (%)	Elastic modulus Modulus (MPa)
0	6.3 ± 0.2	202.0 ± 33.9	100
1.5	6.8 ± 1.5	65.6 ± 2.5	110
3.0	10.6 ± 2.6	43.1 ± 5.6	208
5.6	23.5 ± 2.3	15.9 ± 1.7	320
10	49.8 ± 4.5	10.3 ± 0.3	937

of the hydrogen bonding between the nanowhiskers and PVA chains reducing mobility and resulting in a material with lower elasticity but providing reinforcement to the whole film structure. Similar results were reported by different authors[34-36].

NWCH mechanically reinforce the matrix of PVA but to better understand the reinforcing effect of the NWCH on the PVA nanocomposite films, theoretical values were calculated using two different models. The classical phenomological series-parallel model of Takayanagi et al.[37,38] that accounts for a percolating network where the fillers interact by hydrogen bonding forces above a calculated volume fraction. In this approach the composite elastic tensile modulus, E_c, can be calculated using Equation 2.

$$E_c = \frac{(1-2\cdot\psi+\psi\cdot v_r)\cdot E_S\cdot E_R + (1-v_r)\cdot\psi\cdot E_R^2}{(1-v_r)\cdot E_R + (v_r-\psi)\cdot E_S} \quad (2)$$

where the subscripts R and S refer to a "rigid" phase and a "soft" phase, the reinforcement agent and the matrix, respectively. The parameter Ψ is a correction factor of the nanowhiskers volume fraction enrolled in percolation and can be determined by Equation 3.

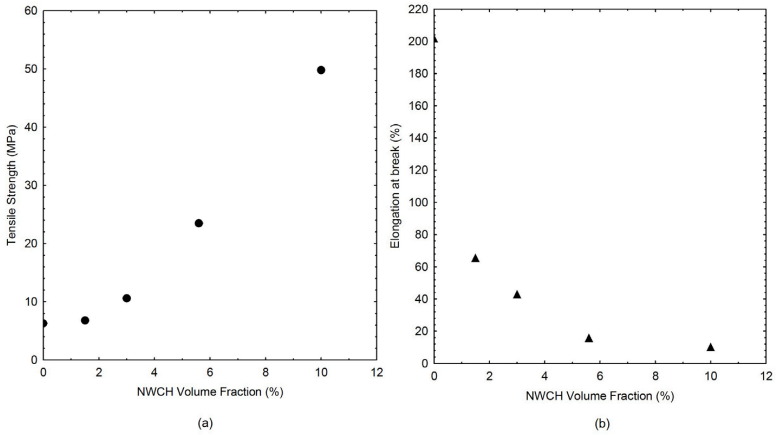

Figure 5. Tensile Strength at break (a) and Elongation at break (b) for each composite with with different nanowhiskers volume fraction.

$$\psi = 0, v_r \le v_{rc}$$
$$\psi = v_r \cdot \left(\frac{v_r - v_{rc}}{1 - v_{rc}} \right)^{0.4}, v_r > v_{rc} \quad (3)$$

Where v_r is the nanowhiskers volume fraction and v_{rc} is the percolation threshold (the lower volume fraction where the percolation phenomena begins). Using this model, above a volume fraction of 4.4%vf a dramatic increase in Elastic modulus's is expected, and should be linked to the percolation phenomena, since it's the calculated percolation threshold for an aspect ratio of 15.9[39]. Above percolation, the establishment of a NWCH network is be responsible for the gradual increase of the elastic tensile modulus. The Halpin-Tsai model[40] was formulated for composites reinforced with well dispersed, continuous and aligned fibers, and modified by Nielsen for short fibers[41]. This model can also predict the elastic tensile modulus using Equation 4.

$$E_C = E_S \frac{1 + \xi B v_r}{1 - \Omega B v_r} \quad (4)$$

where,

$$\xi = 2\frac{L}{D} \quad (5)$$

and,

$$B = \frac{\frac{E_R}{E_S} - 1}{\frac{E_R}{E_S} + \xi} \quad (6)$$

and,

$$\Omega = \frac{1 - \Phi_m}{\Phi_m^2} V_r \quad (7)$$

Using the shape parameter ξ, related to the reinforcement geometry and the load direction, the Halpin-Tsai equations can be used to estimate the elastic tensile module for short fiber reinforcement as proposed. With the parameter Ω the model takes into account the maximum fraction of reinforcement admitted by a composite system, ϕ_m. This value is dependent on the particle geometry and packaging, for example, for a cubic packing ϕ_m takes a value of 0.785 and for hexagonal packing a value of 0.907 is used[42]. These high values are typical of aligned continuous fiber composites. In the case of composites with nanowhiskers as reinforcement, the nanoparticles are arranged randomly, and can take values considerably lower[42]. Due to uncertainty regarding the maximum fraction of reinforcement and its dependence on both the alignment and the aspect ratio of the reinforcement, ϕ_m is used as an empirical adjustment factor in the equations of Halpin-Tsai. The parameters used in boths models are summarized in Table 3.

Table 3. Values used by both models while calculating simulations.

Notation	Parameter	Value
E_S	Elastic tensile modulus of soft phase	100 MPa
E_R	Elastic tensile modulus of rigid phase	2000 MPa[43]
ξ	Shape parameter	31.8 (aspect ratio 15.9)
v_{rc}	Critical volume fraction	4.4%
Φ_m	Adjustment factor	0.17

Analysing Figure 6, the series-parallel model (Percolation) is not in agreement with the values obtained experimentally. It should be noted that this model is widely used for modeling experimental data for composites reinforced with cellulose nanowhiskers. As result, one explanation for the failure in the setting of this model can be the hypothesis of the formation of a percolation network, or the lack of such molecular structure. This network is established due to the formation of links by hydrogen bonds between cellulose nanowhiskers. For chitin nanowhiskers, possibly these links are hampered by the presence of acetyl groups and amine groups on the surface, resulting in lower interactions between chitin microcrystals. The ineffectiveness of the series-parallel model to fit the experimental results can also be related to the fact that the occurrence of a percolation network is either more likely has greater the difference between the Elastic tensile modulus of the matrix and the nanowhisker. Morin and coworkers

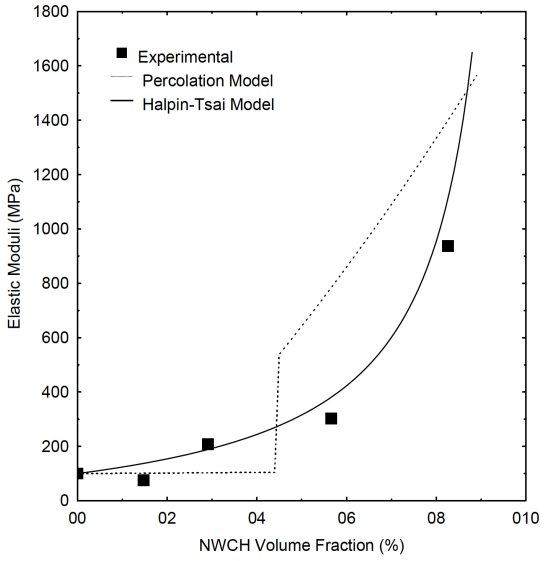

Figure 6. Plot comparing the Halpin-Tsai and Percolation(Series Parallel) models with experimental results.

found that this model was unable to predict the elastic tensile modulus of composite PCL/NWCH, because the difference between the elastic tensile modulus of the matrix and nanowhiskers was not significant[43]. In fact, when the s tensile modulus of the two phases are close (a difference of one order of magnitude or lower) the influence of the percolating rigid phase is negligible at low reinforcement concentrations, such as those used in this work. In this case, the mechanical properties do not suffer an abrupt change, as predicted by the percolation model, and depend on the homogeneity of the composite[44].

Thus, it was used the Halpin-Tsai model in order to predict the composite elastic tensile modulus´s. The values of the parameters used in this model are listed in Table 3. As shown from Figure 6, with Halpin-Tsai equations the obtained values for the elastic tensile modulus are very close to the values obtained experimentally. This suggests that the packing of NWCH plays a more important role reinforcing the polymeric matrix. In fact, good correlation between the experimental values of elastic tensile modulus with those obtained by this model seems to suggest that there is no percolation phenomenon in these composites. The low value of the maximum fraction nanowhiskers used was provided by Nielsen[41,42] for composites with short fibers randomly arranged in space, such as those studied here. Finally, Halpin-Tsai theoretical values assumes perfectly dispersed and homogeneised nanowhiskers on the matrix so, for this reason, small differences between the experimental and theoretical values were obtained[44].

4. Conclusions

In the present work, pure alpha-chitin nanowhiskers were produced and successfully added to thermoplastic PVA films. From the thermal transitions analysis it was concluded that nanowhiskers provided an anti-plastifying effect due to reduced mobility of amorphous and crystalline PVA chains around the nanowhiskers particles resulting in increases of glass transition temperature and melting temperature. Swelling index was also reduced by the inclusion of chitin nanowhisker resulting in films with higher moisture resistance. The tensile tests results presented an increase in the elastic tensile modulus and tensile strength revealing a reinforcement of the mechanical properties. While applying boths model to the elastic tensile modulus experimental results it was clear that the reinforcing mechanism is related to the nanowhiskers packing in the matrix and not to the percolation phenomena as initially thought.

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