

# Effectiveness of Silane Monomer on Chitosan Films and PCL-Based Tri-Layer Films

Nusrat Sharmin, Ruhul A. Khan, Stéphane Salmieri, Dominic Dussault, Monique Lacroix

Research Laboratories in Sciences Applied to Food, Canadian Irradiation Center (CIC), INRS-Institute Armand-Frappier, Institute of Nutraceuticals and Functional Foods, University of Quebec, 531 Boulevard des Prairies, Laval, Quebec H7V 1B7, Canada

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**ABSTRACT:** Chitosan films were prepared by casting from its 1% (w/w) solution. Tensile strength (TS), tensile modulus (TM), and elongation at break (Eb%) of chitosan films were found to be 30 MPa, 450 MPa, and 8%, respectively. Silane monomer (3-aminopropyl tri-methoxy silane) (1–7%, w/w) was added into the chitosan solution (1%, w/w), and films were casted. The highest TS (38 MPa) and TM (620 MPa) values were found at 5% (w/w) silane content films. Polycaprolactone (PCL) films were prepared by compression molding; the values of TS, TM, and Eb of PCL films were found to be 12 MPa, 226 MPa, and 70%, respectively. Using chitosan and silane containing chitosan films, PCL-based tri-layer films were prepared by com-

pression molding. Chitosan (also silane-incorporated chitosan) content in the tri-layer films varied from 10 to 50% by weight. The values of TS and TM of the silane containing composites were found to be 21 and 410 MPa, respectively, which is significantly higher (40% TS and 34% TM) than control composites. Molecular interactions due to silane addition were supported by FT-IR analysis. The surface of the films and the interface of the tri-layer films were investigated by scanning electron microscope (SEM). © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 224–232, 2012

**Key words:** chitosan; PCL; biodegradable films; silane; packaging materials

## INTRODUCTION

Due to the excellent thermo-mechanical properties, petroleum-based synthetic polymers are largely used as packaging materials. These materials can withstand extreme temperatures and are durable, cheap, and easy to use. Unfortunately, these materials are not biodegradable. Thus, efforts are in progress to develop alternative packaging materials that are environment-friendly, cheap, and lightweight, possess good thermo-mechanical properties and provide a good barrier to moisture, gas, and solid transfer. In this regard, organic compounds like chitosan, cellulose, alginate, gelatin, etc., are taken into considerations. Biodegradable films made of these materials do not pose a threat to the environment and are also cost-effective. However, the disadvantages of these films include poor thermo-mechanical properties and a strongly hydrophilic nature. Therefore, many studies are now attempting to overcome these drawbacks to approach physicochemical attributes analogous to those of petrochemical polymers.<sup>1–6</sup>

Chitosan is a modified, natural carbohydrate polymer composed mainly of  $\beta$ -(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units and partially of  $\beta$ -(1,4)-linked 2-deoxy-2-acetamido-D-glucopyranose, a major component of the shells of crustacean such as crab, shrimp, and crawfish and the second most abundant natural biopolymer after cellulose. It is prepared by the alkaline or enzymatic *N*-deacetylation of chitin which is found in the outer shells of crabs, prawn, shrimp, lobsters, etc. Chitosan contains a large number of hydroxyl and amino groups. These two functional groups provide several possibilities for grafting of desirable bioactive groups. Chitosan is largely studied in pharmaceutical and medical fields for its biodegradability, biocompatibility, bioactivity, and its interesting physicochemical properties. Chitosan could be used to prepare biodegradable packaging materials. Because of its hydrophilic nature and poor water endurance, technical applications of chitosan remain limited. However, the hydrophobicity of the chitosan films can be increased by blending it with some synthetic polymers which are strongly hydrophobic in nature.<sup>7–12</sup>

Recently, aliphatic polyesters have attracted much research interest due to their biodegradability and biocompatibility. Poly(caprolactone) (PCL) is one of the typical aliphatic polyesters, and it is fully biodegradable, biocompatible, and nontoxic to living organisms. PCL is prepared by ring opening polymerization of  $\epsilon$ -caprolactone using a catalyst such as

Correspondence to: M. Lacroix (monique.lacroix@iaf.inrs.ca).

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stannous octanoate.<sup>13–15</sup> PCL has good resistance to water, oil, solvent, and chlorine. The unique properties of PCL render its potential in biomedical fields, and it has been used in the development of controlled drug delivery systems, as well as in surgical sutures and other resorbable fixation devices. One of the main commercial applications of PCL is in the manufacture of biodegradable films. The melting point of PCL is about 60°C. The molecular weight of PCL greater than 40,000 can be melt processed into strong water-resistant films.<sup>16,17</sup>

Silane coupling agents belong to a class of organo-silane compounds having at least two reactive groups of different types bonded to the silicon atom in a molecule. These materials are used as promoters, dispersing agents, cross-linking agents, surface modifiers, etc. Alkoxysilanes such as 3-aminopropyl tri-methoxy silane (APTMS) are used for coupling organic polymer and inorganic filler, thus improving the properties of the products, such as bending strength, physical mechanical properties, electrical properties, water resisting property, and anti-aging property. As a cross-linking agent, it is used in various polymers like polyethers, polyurethanes, polyesters, etc. When used in thermoplastic and thermosetting resin such as phenol aldehyde, polyester, epoxy, PBT, polyamide, carbonic ester, it can greatly improve dry and wet bending strength, compression strength, shear strength, and other physical mechanical properties and wet electric properties, also improve the wetting property and dispersion of stuffing into polymer.<sup>18,19</sup>

The objective of the present research was to fabricate chitosan films reinforced with PCL-based tri-layer insoluble films for packaging and also to evaluate the effect of silane coupling agent on chitosan and tri-layer films. The mechanical properties of the films were measured to evaluate their tensile strength (TS), tensile modulus (TM), and elongation at break (Eb%). Water vapor permeability (WVP) tests were carried out to investigate the moisture barrier properties of the films. Molecular interactions due to silane addition were investigated by FTIR analysis. Surface of chitosan films and the interface of tri-layer films were investigated by scanning electron microscope (SEM).

## MATERIALS AND METHODS

### Materials

Chitosan (Kitomer,  $M_w$  1600 kDa, 85–89% deacetylation degree) was obtained from Marinard Biotech Inc. (Rivière-aux-Renards, QC, Canada). (3-Aminopropyl)-trimethoxysilane and PCL (granules form, molecular weight: 80,000) was purchased from Sigma-Aldrich Canada, Ltd. (Oakville, ON, Canada).

### Methods

#### Film preparation

Aqueous chitosan solution (1%, w/w) was prepared using acetic acid solution (2%, w/w). Films of chitosan were prepared by casting at room temperature and at 35% relative humidity (RH). For the preparation of silane-coupled chitosan films, silane was added at a concentration of 1–7% (w/w) to chitosan solution and films were cast in the same process. Dried films (thickness was around 100  $\mu\text{m}$ ) were peeled off manually and stored in polyethylene bags prior to characterization and tri-layer film fabrication.

#### Composite fabrication

To make PCL sheets, granules of PCL (about 5 g) were placed into two steel plates and placed in the heat press (Carver Inc., USA, Model 3856). The press was operated at 80°C. Steel plates were pressed at 500 kPa pressure for 2 min. The plates were then cooled for 1 min in a separate press under same pressure at room temperature. The resulting PCL film (thickness was around 100  $\mu\text{m}$ ) was cut into the desired size (120 mm  $\times$  80 mm) for tri-layer films fabrication. Tri-layer films were prepared by sandwiching one layer of chitosan and silane (5% w/w)-coupled chitosan film between two sheets of PCL. The resulting sandwich was then heated at 80°C for 3 min to soften the polymer (PCL) prior to pressing at 100 kPa pressure. The plates were then cooled for 2 min in a separate press under same pressure at room temperature. The chitosan weight fractions in the tri-layer film were varied from 10–50% by weight. Weight fraction of chitosan (termed as chitosan content) was varied in tri-layer films by controlling the thickness of PCL films. The dimension of the tri-layer films was 120 mm  $\times$  80 mm  $\times$  0.2 mm.

#### Measurement of the mechanical properties

Tensile strength (TS), tensile modulus (TM), and elongation at break (Eb%) of the films were measured by Universal Tensile Machine (UTM) (Tinius-Olsen Inc., USA, Model H5K) using a 1 kN load cell, with a crosshead speed of 1 mm/s at a span distance of 25 mm. The dimensions of the test specimen were (ISO 14125) 60 mm  $\times$  15 mm  $\times$  0.2 mm, according to the ASTM test D638-99.

#### Water uptake of the composite films

Water uptake test of composite films was carried out in deionized water at room temperature (25°C). This test was carried out up to 144 h. Composite samples were taken into glass beakers containing 100 mL of

**TABLE I**  
**Effect of Silane on the Tensile Properties of Chitosan Films**

Composition	Tensile strength (MPa)	Tensile modulus (MPa)
Chitosan (100%)	30 ± 0.5 <sup>a</sup>	450 ± 10 <sup>a</sup>
Chitosan (99%) + Silane (1%)	31 ± 0.4 <sup>b</sup>	492 ± 8.8 <sup>b</sup>
Chitosan (98%) + Silane (2%)	33 ± 0.3 <sup>c</sup>	536 ± 11.4 <sup>c</sup>
Chitosan (97%) + Silane (3%)	35 ± 0.4 <sup>d</sup>	571 ± 9.6 <sup>d</sup>
Chitosan (96%) + Silane (4%)	36 ± 0.5 <sup>e</sup>	598 ± 10.3 <sup>e</sup>
Chitosan (95%) + Silane (5%)	38 ± 0.4 <sup>f</sup>	622 ± 9.3 <sup>f</sup>
Chitosan (94%) + Silane (6%)	33 ± 0.3 <sup>c</sup>	580 ± 11.0 <sup>d</sup>
Chitosan (93%) + Silane (7%)	29 ± 0.5 <sup>a</sup>	553 ± 10.4 <sup>c</sup>

Means followed by the same letter are not significantly different at the 5% level.

deionized water. At set time points, samples were taken out and wiped out properly and then reweighed and measured as water uptake values.

#### Water vapor permeability (WVP) test

The WVP test was conducted gravimetrically using a modified procedure from ASTM test 15.09: E96. Films were mechanically sealed onto Vapometer cells (No. 68-1, Twining-Albert Instrument Company, West Berlin, NJ, USA) containing 30 g of anhydrous calcium chloride (0% RH). The cells were initially weighed and placed in a Shellab 9010L controlled humidity chamber (Sheldon Manufacturing Inc., Cornelius, OR) maintained at 25°C and 60% RH for 24 h. The amount of water vapor transferred through the film and absorbed by the desiccant was determined from the weight gain of the cell. The assemblies were weighed initially and after 24 h for all samples and up to a maximum of 10% gain. Changes in weight of the cell were recorded to the nearest 10<sup>-4</sup> g. WVP was calculated according to the combined laws of Fick and Henry for gas diffusion through coatings and films, according to the equation:

$$\text{WVP}(\text{g}\cdot\text{mm}/\text{m}^2\cdot\text{day}\cdot\text{kPa}) = \Delta wx/A\Delta P,$$

where  $\Delta w$  is the weight gain of the cell (g) after 24 h,  $x$  is the film thickness (mm),  $A$  is the area of exposed film ( $31.67 \times 10^{-4} \text{ m}^2$ ), and  $\Delta P$  is the differential vapor pressure of water through the film ( $\Delta P = 3.282 \text{ kPa}$  at 25°C).

#### FT-IR spectroscopic analysis

FTIR spectra of the films were recorded using a Spectrum One spectrophotometer (Perkin-Elmer, Woodbridge, ON, Canada) equipped with an attenuated total reflectance (ATR) device for solids analysis and a high-linearity lithium tantalate (HLLT) detector. Spectra were analyzed using Spectrum 6.3.5 software. Films were stored at room temperature for 72 h in a desiccators containing saturated NaBr solution to

ensure a stabilized atmosphere of 59.1% RH at 20°C. Films were then placed onto a zinc selenide crystal, and the analysis was performed within the spectral region of 4000–650 cm<sup>-1</sup> with 64 scans recorded at a 4 cm<sup>-1</sup> resolution. After attenuation of total reflectance and baseline correction, spectra were normalized with a limit ordinate of 1.5 absorbance units. The resulting FTIR spectra were compared to evaluate the effects of silane coupling on chitosan based on the intensity and shift of vibrational bands.

#### Scanning electron microscopic (SEM) analysis

Film samples (5 × 5 mm) were deposited on an aluminum holder and sputtered with gold-platinum (coating thickness, 150–180 Å) in a Hummer IV sputter coater. SEM photographs were taken with a Hitachi S-4700 FEG-SEM scanning electron microscope (Hitachi Canada Ltd., Mississauga, ON, Canada) at a magnification of 40,000×, at room temperature. The working distance was maintained between 15.4 and 16.4 mm, and the acceleration voltage used was 5 kV, with the electron beam directed to the surface at a 90° angle and a secondary electron imaging (SEI) detector.

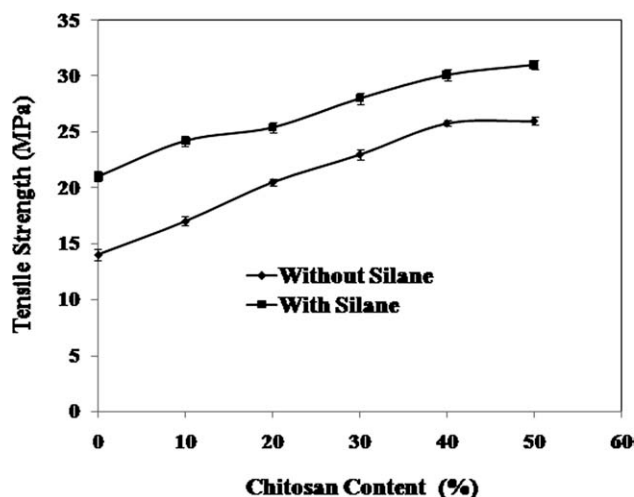
#### Statistical analysis

For each measurement, three replicate samples were tested. Analysis of Duncan's multiple-range tests were used to perform statistical analysis on all results, using PASW Statistics Base 18 software (SPSS Inc., Chicago, IL, USA). Differences between means were considered to be significant when  $P \leq 0.05$ .

## RESULTS AND DISCUSSION

### Effect of silane on the tensile properties of chitosan films

The values of TS and TM of the silane treated films are tabulated in Table I. It is clear that TS values increased due to the incorporation of silane and showed highest value of 38 MPa at the 5% silane



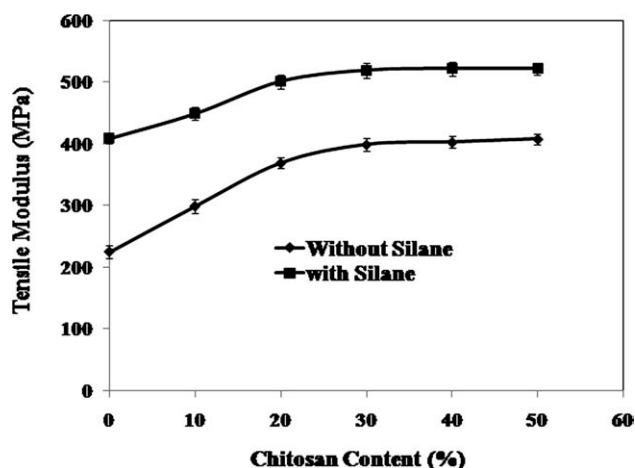
**Figure 1** Tensile strength of the composite films containing pure chitosan and silane (5% w/w)-coupled chitosan against chitosan content in the composite.

content. The TS value increased up to the concentration of 5% and then decreased with an increase of silane concentration, which could be due to homopolymerization reaction of silane molecules into polysiloxane. At low concentration of silane, reaction between chitosan and silane might be dominated but at higher silane concentration, the reaction is hindered but the reaction between siloxanes (homopolymerization reaction) occurred and thus formed polysiloxane.<sup>13</sup> The TM of the films followed the similar trend like the values of TS. A 5% silane-contained chitosan films showed the highest TM, which is 620 MPa and about 38% higher than that of pure chitosan films. From this investigation, this is clearly evidenced that silane-coupled chitosan films showed higher TS and TM over the pure chitosan films. Silane is a universal coupling agent for all types of fibers and is effective with all polymeric matrices.<sup>8</sup> Silane forms silanols in aqueous medium and then reacts with the hydroxyl group of the chitosan in aqueous media, via hydrogen bonding, which could explain these improved mechanical properties.<sup>19</sup>

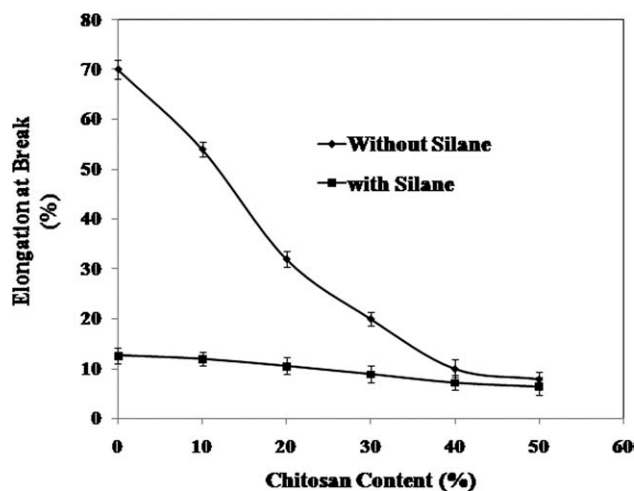
#### Effect of chitosan on the tensile properties of tri-layer films

The effect of silane content on TS values of the chitosan reinforced PCL-based tri-layer films is shown in Figure 1. Here, TS values of the films are plotted against the chitosan content in the tri-layer films. The chitosan content in the films varied from 10 to 50% by weight. The maximum TS values of the control films (chitosan reinforced PCL-based tri-layer film) and silane-based tri-layer films (silane containing chitosan film reinforced PCL-based films) were found to be 26 and 31 MPa for 50% chitosan content, respectively. Indeed, it was observed that the incor-

poration of silane allowed significant and progressive improvements of the TS values. At 10% chitosan addition, TS values of the silane containing chitosan-based tri-layer films were increased by 50% as compared to the control films. Then, TS values were improved by 42, 24, 22, and 20%, respectively, for 20, 30, 40, and 50% chitosan addition in the silane-based tri-layer films, suggesting a lower progressive improvement rate. These increased TS values of the silane films were due to the presence of silane monomer. The silane coupling agent used here has the formula  $[H_2N(CH_2)_3-Si-(OCH_3)_3]$ . The methoxy groups ( $-OCH_3$ ) are hydrolyzed in the presence of aqueous media. In this context, hydrolyzed silane could undergo a condensation reaction with the naturally occurring hydroxyl group on the chitosan. The surface of chitosan film could therefore be covered by a silane network through oxane bonds with the chitosan surface.<sup>19</sup> These statements could support the fact that this silane bridge improves the adhesion between chitosan and PCL in the silane-based films. Pluedemann<sup>20</sup> suggested that all silane coupling agents tend to be effective with all organic resins. Jiang et al.<sup>21</sup> reported that E-glass fiber surface was reacted with PCL through *in situ* polymerization. Thus, a significant improvement found in the TS values of silane-based tri-layer films as compared to control films which could be due to the presence of silane. Figure 2 shows the effect of silane content on TM values of chitosan reinforced PCL-based tri-layer films. It was found that the maximum TM values of control films and silane containing films were 400 and 520 MPa, respectively (for 30% chitosan content). Here, TM values of the films are plotted against the chitosan content in the tri-layer films. The TM values of silane films were much higher than control composite films. An improvement of 81, 47, 36, 30, 30, and 29% was observed in the TM



**Figure 2** Tensile modulus of the composite films containing pure chitosan and silane (5% w/w)-coupled chitosan against chitosan content in the composite.



**Figure 3** Elongation at break of the composite films containing pure chitosan and silane (5% w/w)-coupled chitosan against chitosan content in the composite.

values of silane films as compared to control films for 10, 20, 30, 40, and 50% chitosan content, respectively. The TM values of control tri-layer films were lower because of the fact that chitosan is strongly hydrophilic and PCL is strongly hydrophobic. Thus, the interfacial adhesion between chitosan and PCL is very poor. Improvement in the TM values of the silane-based tri-layer films could be due to cross-linking between the hydroxyl group of chitosan and amino group of silane. Again, it could be assessed that silane improves the interfacial adhesion between chitosan and PCL. For comparison, Khan et al.<sup>18</sup> reported that vinyl-trimethoxy silane (VTMS)-grafted gelatin films showed higher TM values due to the cross-linking between amino group of gelatin and vinyl group of (VTMS). Flexibility and elasticity of the blend films are essential parameters that are considered during the application of the polymer. These two phenomena are related to the elongation at break of the film. The results of Eb values of silane treated and untreated composite films are plotted in Figure 3. It is clear from the figure that there was a monotonous decrease in the Eb values for both silane treated and untreated tri-layer films with the increased chitosan content. The decreased Eb values may be related to the increased stiffness of the composite films by the addition of chitosan films. But silane-treated composite films showed much lower Eb than the untreated composite films. For 10% chitosan addition, Eb values of silane treated and untreated tri-layer films were found to be 70 and 13%, respectively. Thus, the Eb values of the silane treated films were 82% lower than the untreated composite films. This may be attributed to the fact that the cross-linking behavior of silane stiffens chitosan. Han et al.<sup>22</sup> reported that the introduction of crosslinking structure into PLLA chains

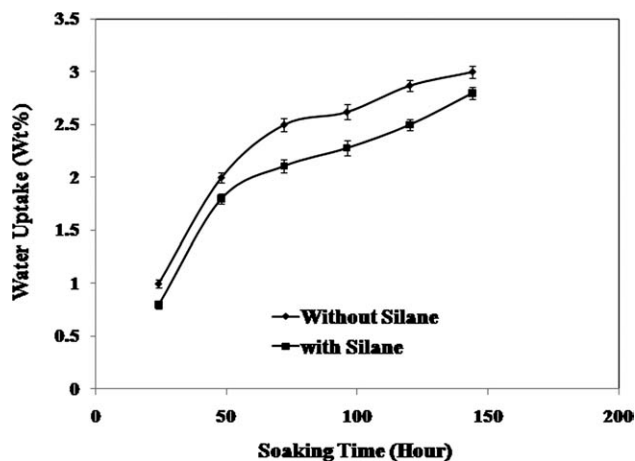
results in an increase of tensile strength and decrease of elongation at break. Thus, in our experiment silane contributes brittle character and lowers Eb.

### Water uptake of the tri-layer films

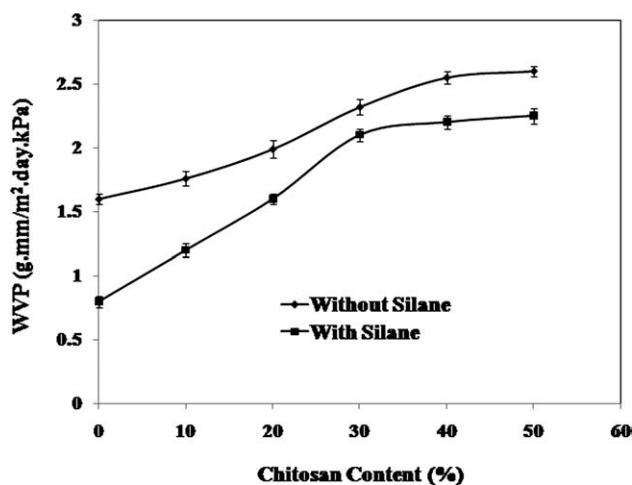
Water uptake of the tri-layer films (chitosan and silane-treated chitosan reinforced PCL based) was investigated up to 144 h (6 days) and results are shown in Figure 4. Both treated and untreated composite films showed similar trend in the water uptake kinetics, i.e., initial rapid water uptake followed by almost constant water uptake over the remaining time. It is clear that for both treated and untreated trilayer films, water uptake values seemed to increase slowly even after 48 h of the soaking time. Then, both types of films have reached a limit water uptake of 3% and 2.8% after 144 h, for untreated and silane-treated films, respectively. Since PCL is strongly hydrophobic in nature and the upper and lower layers of the tri-layer films were composed of PCL, chitosan absorbed water through the cutting edges. That is why the percentage water uptake of the tri-layer films was so low to a value. However, the percentage of water uptake in both types of films remained almost similar over time.

### Water vapor permeability (WVP)

WVP is a measure of ease of the moisture to penetrate and pass through a material. In a preliminary study, WVP of PCL, chitosan, and silane grafted chitosan films were found to be 1.5, 4.7, and 3.2 g.mm/m<sup>2</sup>.day.kPa, respectively. The WVP values of chitosan films decreased as silane was incorporated. It is known that the free hydroxyl and amino groups on



**Figure 4** Water uptake of the composite films containing pure chitosan and silane (5% w/w)-coupled chitosan against chitosan content in the composite.



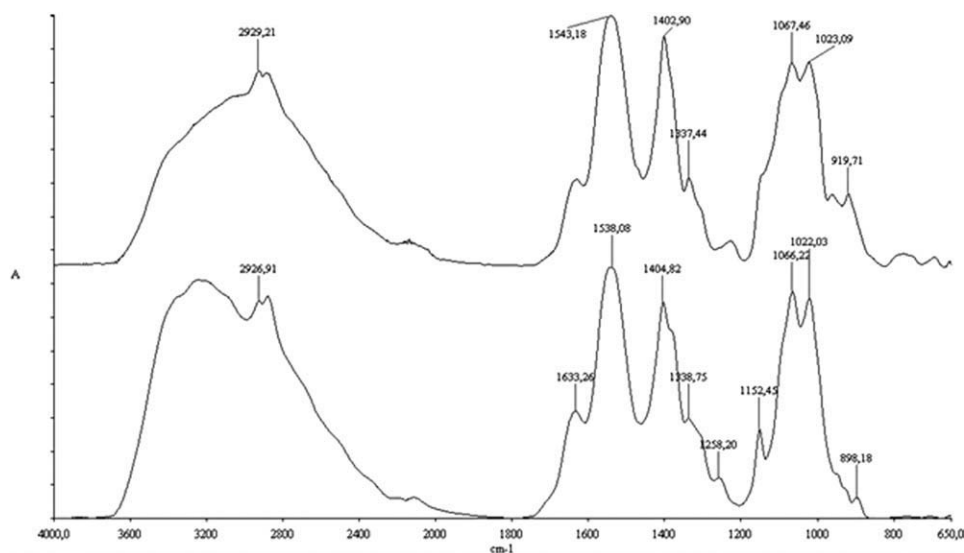
**Figure 5** Water vapour permeability of the composite films containing pure chitosan and silane (5% w/w)-coupled chitosan against chitosan content in the composite.

chitosan are hydrophilic. The decrease in the WVP for the crosslinked chitosan films may possibly be due to the consumption of the hydroxyl group on the chitosan after cross-linking. The effect of chitosan content on WVP of tri-layer films is shown in Figure 5. It is clear that the values of WVP of the silane treated tri-layer films are lower than that of the untreated films. It is reported<sup>23</sup> that the water vapor barrier properties of chitosan films were improved significantly by the addition of cellulose nano fibers. Although silane treated composite films have a lower WVP, both films with and without silane present a similar profile of WVP evolution in function of chitosan content increase. Owing to the large amount of hydrogen bonds, most of the bio-polymeric films are strongly hydrophilic, that is respon-

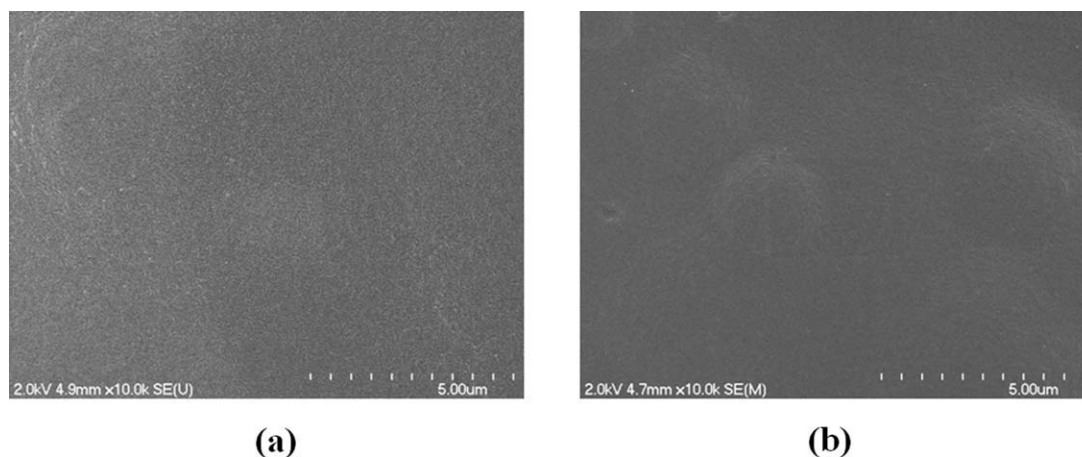
sible for poor barriers to water vapor.<sup>24–26</sup> The presence of chitosan in the PCL-based composites is responsible for slightly higher WVP values compared to PCL films. In our present study, composites are made of tri-layers (PCL/chitosan/PCL). In the present study, PCL is used as the composite matrix which is responsible for the lower water vapor barrier properties of the composite as compared to the chitosan. So, with the rise of chitosan content in tri-layer films, the WVP values moved toward the WVP values of chitosan.

### FT-IR analysis

Figure 6 shows FTIR spectra of chitosan (a) and silane-treated chitosan (b) films. The absorption peaks of pure chitosan films are mainly assignable to (i) the stretching intra- and intermolecular O—H vibrations at 3500–3200 cm<sup>-1</sup>, overlapped with amine and secondary amide stretching mode, (ii) symmetric and asymmetric C—H vibrations at 2930–2850 cm<sup>-1</sup>, (iii) Amide I vibrational mode (acetamido group) at 1633 cm<sup>-1</sup>, and (iv) Amide II (amino group) at 1538 cm<sup>-1</sup>.<sup>27</sup> The two peaks at 1066 and 1022 cm<sup>-1</sup> are the result of the saccharide structure of chitosan which was already reported by Bhattarai et al.<sup>28</sup> Another typical peak at 1339 cm<sup>-1</sup> is characteristic of —CH<sub>3</sub> symmetrical deformation mode whereas the band at 1152 cm<sup>-1</sup> is related to asymmetric stretching of C—O—C linkage in saccharide residue. The silane grafted chitosan spectrum (b) shows that the region 3500–3200 cm<sup>-1</sup>, associated with —OH groups of chitosan, was weakened and shifted to higher wavenumbers with silane content in the film, suggesting a significant reduction —OH groups and intermolecular hydrogen bonding in chitosan-Si matrix after



**Figure 6** FTIR spectra of chitosan (a) and silane (5% w/w)-coupled chitosan films (b).



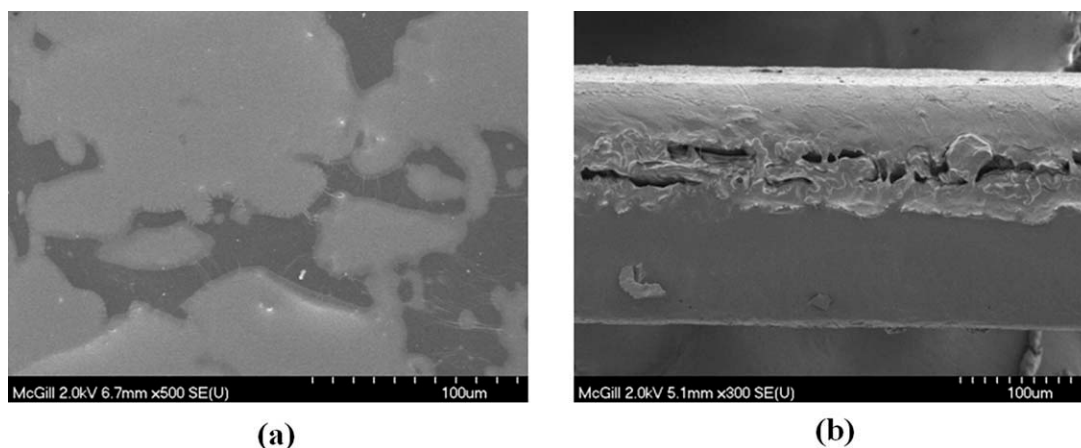
**Figure 7** Scanning electron microscopic (SEM) image of the surface of chitosan film (a) and the surface of 5% silane coupled (b) chitosan film.

reaction. In the presence of moisture, hydrolyzable alkoxy group leads to the formation of silanols that can react with hydroxyl groups from chitosan via self-condensing polymerization, as described by Liu and Zhang and Agrawa et al.<sup>29</sup> Therefore, the hydrocarbon chains provided by the application of silane restrain the swelling of the fiber by creating a cross-linked network because of covalent bonding between the matrix and the fiber.<sup>30</sup> It is also interesting to note that a modification resulted in stretching C—H vibrations at 2930–2850  $\text{cm}^{-1}$ , with an inverted intensity of methyl compared to methylene bands after treatment with silane. Indeed, the introduction of silane into the chitosan leads to (i) an increase at 2929  $\text{cm}^{-1}$  corresponding to methylene groups from aminopropyl branch of silane and (ii) a decrease at 2843  $\text{cm}^{-1}$  related to methyl groups from methoxysilane functional groups (Si—OCH<sub>3</sub>).<sup>31</sup> A reduced intensity was also observed at 1258  $\text{cm}^{-1}$ , in relation with C—O—C anti-symmetric stretch from esters related to acetyl group from chitosan or C—OH in plane bend vibration, both mentioned as reacting groups with silane. As a silylation effect, a correlated trend was noted with the disappearance of the band at 1152  $\text{cm}^{-1}$  related to C—O—C steric hindrance of anhydroglucose unit of chitosan related to silane coupling.<sup>29</sup> In addition to this effect, a resulting broaden band was thereby observed around 1152–1023  $\text{cm}^{-1}$  probably owing to Si—O—C or Si—O—Si antisymmetric stretching vibrations in siloxanes.<sup>19</sup> In order to assess more precisely the presence of silane into chitosan matrix, two particular bands appeared after chitosan-Si reaction at 1224 and 776  $\text{cm}^{-1}$ , corresponding to C—C—N bending in aminopropyl group and to —CH bending in alkyl group from silane, respectively. Similar observations were reported by Liu and Zhang<sup>29</sup> and Panaitescu et al.<sup>32</sup> for silylation reactions of cellulose fibers. Finally, the absorp-

tion band at 919  $\text{cm}^{-1}$  was assigned to Si—OH stretching vibration related to silanol groups that did not react with chitosan. Hence, from all these considerations, it is clear that the addition of silane into chitosan films involved significant structural modifications in relation with chitosan-Si interactions.

#### Scanning electron microscopic analysis (SEM)

Surface of the chitosan films and silane-coupled chitosan films was investigated by SEM and micrographs are presented in Figure 7. The micrograph of pure chitosan film showed a rough and irregular surface [Fig. 7(a)]. The silane-coupled chitosan films showed a homogenous, smoother, and denser film surface with no gross defects [Fig. 7(b)]. These films were also free of bubbles as compared to pure chitosan films. For silane-treated films, a polysiloxane coating formed which might be responsible for the smooth surface. The smooth and homogenous surface of the films is an indicator of the structural integrity of the observed films, and thus explaining good mechanical properties that were obtained in relation with a better solubilization and homogenization of chitosan and silane monomer in aqueous solution. The surface of degraded chitosan and interface of tri-layer (chitosan-PCL-chitosan) films were also investigated and presented in Figure 8. Chitosan films were rapidly degraded in aqueous medium since the films contained acetic acid. The chitosan films were immersed in water for just 2 min then dried in an oven for 1 h at 110°C. SEM image [Fig. 8(a)] indicated that a fraction of the films dissolved. On the other hand, the interface of the tri-layer films [Fig. 8(b)] indicated that a partial dissolution started after 6 days of immersion in water. Upper and lower part indicated intact surface which is PCL parts but the middle layer is chitosan (30% chitosan and 70%



**Figure 8** Scanning electron microscopic (SEM) image of the surface of partially dissolved chitosan film (a) and interface (b) of the composite films.

PCL) which started to degrade in water. Promising information was found from these SEM images. Chitosan films are soluble in water but when coated with PCL (in tri-layer films), the degradation is significantly hindered.

### CONCLUSIONS

Biodegradable chitosan films were prepared by solution casting and PCL films were prepared separately by compression molding. Then, PCL-chitosan-PCL-based biodegradable tri-layer films were prepared successfully by compression molding. Silane was incorporated into the chitosan films and found better mechanical properties. Chitosan content in the composite varied from 10–50% by weight. It was found that silane contributed significantly ( $P = 0.05$ ) to the improvement of mechanical properties of the composites. With an increase of silane content (up to 5%, w/w), a significant improvement ( $P = 0.05$ ) in the tensile properties and water vapor barrier properties were observed. SEM analysis of surface morphology of chitosan films and silane containing chitosan films provided justification of the improved properties obtained by the addition of silane, based on a homogenous, denser and more ordered structure. Moreover, FTIR analysis allowed characterizing the effect of silane coupling on chitosan via film formation, suggesting strong polymer–monomer interactions. From all these supported measurements, silane was found to be a very good coupling agent in chitosan reinforced PCL-based biodegradable composite films. Therefore, further investigations that could allow improving silane-chitosan reactivity would be appropriate in order to manufacture composite materials with enhanced functional properties.

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