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Fabrication and Characterization of Biodegradable Composite Films Made of Using Poly(caprolactone) Reinforced with Chitosan

Nusrat Sharmin · Ruhul A. Khan · Stephane Salmieri · Dominic Dussault · Monique Lacroix

Abstract Chitosan was dissolved in 2 % aqueous acetic acid solution and the films were prepared by solution casting. Values of tensile strength (TS), tensile modulus (TM), elongation at break (Eb %) and water vapor permeability (WVP) of the chitosan films were found to be 30 MPa, 450 MPa, 8 % and 4.7 g mm/m^2 day kPa, respectively. Poly(caprolactone) (PCL) films were prepared from its granules by compression molding and the values of TS, TM, Eb and WVP were 14 MPa, 220 MPa, 70 % and 1.54 g mm/m^2 day kPa, respectively. PCL was reinforced with chitosan films, and composite films were prepared by compression molding. Amount of chitosan in the composite films varied from 10 to 50 % (w/w). It was found that with the incorporation of chitosan films in PCL, both the values of TS and TM of composite films increased significantly. The highest mechanical properties were found at 50 % (w/w) of chitosan content. The Oxygen transmission rate (OTR) of composite film was found to decrease significantly than PCL films. Thermal properties of the composite were also improved as compared to PCL. The water uptake test of the composite also showed promising results with a good stability of composite films. The interface of the composite was investigated by scanning electron microscopy and showed good interfacial adhesion between PCL and chitosan films.

Keywords Biodegradable films · Composites · Chitosan · Packaging materials · PCL · Compression molding

Introduction

With the technological advancement, the use of petroleum-based synthetic polymers as packaging materials is becoming popular since these materials can withstand extreme temperatures, are durable, cheap and easy-to-use. Unfortunately, these materials are not biodegradable. In response to public concern about the effects of not biodegradables on the environment, legislation is being enacted or is pending in many countries to ban non-degradable packaging materials. Thus, efforts are in progress to develop alternative packaging materials that are environment friendly, cheap, light weight, possess good thermo-mechanical properties, and provide a good barrier to moisture and gas. Currently, however, various techniques for producing biodegradable packing materials are being explored, developed, and marketed. In this regard, organic compounds like chitosan, cellulose, gelatin, etc. are taken into considerations. Biodegradable films made of these materials are cost effective and do not pose a threat to the environment. But, the thermo-mechanical properties of these films are very poor and these films are strongly hydrophilic in nature. Therefore, many studies are now attempting to overcome these drawbacks to approach physicochemical attributes analogous to those of petrochemical polymers [1–6].

Chitosan is a biopolymer which is found abundantly in nature and could be used to prepare biodegradable packaging materials. Chitosan is a linear high molecular weight polysaccharide composed mainly of β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units and partially of β-

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(1,4)-linked 2-deoxy-2-acetamido-D-glucopyranose. It is prepared by the alkaline or enzymatic N-deacetylation of chitin which is found in the outer shells of crabs, prawns, shrimps, lobsters, etc. Chitosan contains a large number of hydroxyl and amino groups. Chitosan is reported to be non-toxic, biodegradable, and biocompatible [7–13].

Polycaprolactone (PCL) is a versatile synthetic biodegradable polymer with low melting point (60 °C) which allows easy processing. PCL is prepared by ring opening polymerization of ε-caprolactone monomer using a catalyst such as stannous octanoate [14–17]. One of the main commercial applications of PCL is in the manufacture of biodegradable films. PCL is also used in different biomedical applications [18–21]. PCL was blended with various amorphous [22] and crystalline polymers [23, 24] including chitosan [25] to improve the mechanical properties.

The aim of the present research was to fabricate PCL-based composite films reinforced with chitosan for packaging applications. Fully biodegradable and insoluble composite films were prepared using PCL (synthetic polymer) and chitosan (natural polymer). The potentiality of chitosan films, as reinforcing agent, was studied. The mechanical properties of the composite films were measured to evaluate their tensile strength (TS), tensile modulus (TM) and elongation at break (Eb%). Water vapor permeability (WVP) and Oxygen transmission rate (OTR) tests were carried out to investigate the moisture and oxygen barrier properties of the films in specific conditions. Thermal properties of PCL and composite films were also measured to compare the onset, glass point and offset temperatures of PCL and composite. Interface morphologies of the composite were investigated by scanning electron microscope (SEM).

Materials and Methods

Materials

Chitosan from crab shells (practical grade, powder form; viscosity of 200 cPs) and PCL (granules form, molecular weight: 70,000–80,000) were purchased from Sigma-Aldrich Canada Ltd (Oakville, ON, Canada).

Methods

Film Preparation

At first, 1 % chitosan solution (w/w) was prepared using 2 % (w/w) acetic acid solution. Films of chitosan were prepared by casting the chitosan solution onto flat silicon-coated Petri dishes and allowed to dry for 24 h, at room temperature and at 35 % relative humidity (RH). Dried films were peeled off manually using spatula and stored in polyethylene bags prior to characterization. Thickness of films was maintained to 100 μm.

Composite Fabrication

To make PCL sheets, granules of PCL were placed into two steel plates and then the plates containing PCL were 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 varied in the range of 100–200 μm, depending on composite) was cut into the desired size (120 mm × 80 mm) for composite (tri-layers) film fabrication. The composite was prepared by sandwiching one layer of chitosan film (thickness was around 100 μm) 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 to 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 composite films was 120 mm × 80 mm × 0.2 mm (length × width × thickness). The resulting composites were cut into the desired size and then stored in polyethylene bags.

Measurement of the Mechanical Properties

The films were cut into dog bone shapes using a 10 × 64 mm dog bone cutter. Mechanical properties (TS, TM and Eb) of the films (PCL, chitosan, and composite) were evaluated by using the Hounsfield series S testing machine (UK, H50 KS-0404, Software-QMAT) with a crosshead speed of 1 mm s^{-1} at a span distance of 25 mm. The values of TS, TM, and Eb were calculated from experimental data according to the European standard (ISO/DIS 527-1:2010).

Water Vapor Permeability (WVP) Test

The WVP test was conducted gravimetrically using an ASTM procedure [26]. Films were mechanically sealed onto Vapometer cells (No. 68-1, Twhing-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, USA) 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^{-4} g. WVP was calculated according to the combined laws of Fick and Henry for gas diffusion through coatings and films, according to the equation:

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

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

Oxygen Transmission Rate (OTR)

The OTR was measured using an OX-TRANS® 1/50 (MOCON®, Minneapolis, USA) machine. During all experiments, temperature and relative humidity were held at 23 °C and 0 % RH. The experiments were done in duplicate and the samples (dimension: 50 cm^2) were purged with nitrogen for a minimum of 2 h, prior to exposure to a 100 % oxygen flow of 10 mL/min.

Thermal Properties

Thermal analysis of the PCL and composites was carried out by using the thermo-mechanical analyzer (Linseis TMA, L-77, USA). The dimension of test specimen was: 10 mm × 10 mm × 0.2 mm.

Scanning Electron Microscopy Analysis (SEM)

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.

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 48 h. Composite samples were taken into glass beakers containing 100 ml of deionized water. At set time points, samples were taken out and wiping out properly and then reweighed and measured water uptake values.

Statistical Analysis

For each measurement, three samples in each replicate were tested. Analysis of variance and 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

Measurement of the Mechanical Properties

Tensile Strength (TS)

The effect of chitosan content on TS values of the PCL-based composite films is shown in Fig. 1. Here, TS values of composite films are plotted against the chitosan content in the composite. The TS values of the chitosan and PCL films were found to be 30 and 14 MPa, respectively. Chitosan film was incorporated inside PCL to increase the mechanical properties of the PCL-based composite films. The chitosan content in the composite films varied from 10 to 50 % by weight. With the increase of chitosan content, the TS values of the composite films showed significant improvement ($p \leq 0.05$). At 10 % chitosan addition, TS values of the composite films were increased by 22 %. The TS values were improved by 47, 68, 84 and 86 %, respectively for 20, 30, 40 and 50 % chitosan addition. Improvement in the TS values of the composite films was due to the higher TS value of chitosan (30 MPa) as compared to PCL (14 MPa). So, chitosan films acted as a reinforcement agent in the composite films. The TS values
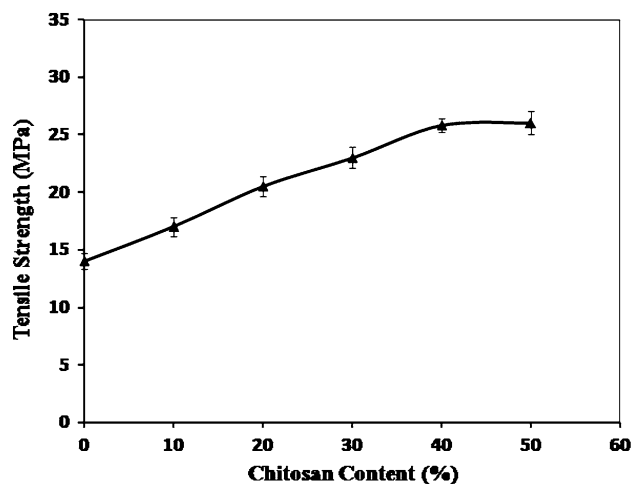

Fig. 1 Tensile strength of the composite films against chitosan-based film content in PCL

were reached to plateau at 40 % chitosan content. There were no significant differences ($p > 0.05$) of TS values between 40 and 50 % chitosan content in the composites. So, further increase of chitosan in composites was not carried out. This could be due to the poor interfacial adhesion between chitosan and PCL. Chitosan is strongly hydrophilic and PCL is strongly hydrophobic, which attributes to the poor interfacial adhesion between each other. Generally, fibers are used as reinforcing agent in conventional composites. In this investigation, one chitosan film was sandwiched between PCL films by compression molding. Chitosan film was found to be a very good reinforcing agent for PCL.

Tensile Modulus (TM)

It was found that the TM values of chitosan and PCL films were 450 and 220 MPa, respectively. Figure 2 shows the effect of chitosan content on TM values of PCL-based composite films. Here, TM values of composite films are plotted against the chitosan content in the composite. With the incorporation of chitosan, the TM values of the composite films showed significant improvement ($p \leq 0.05$). The highest TM value was observed at 50 % chitosan addition. The TM values of the composite films improved by 33, 63, 77, 79 and 81 % for 10, 20, 30, 40 and 50 % chitosan content, respectively. The TM values of the composites found to reach plateau at 30 % chitosan content. No significant ($p \leq 0.05$) differences of TM values were observed after 30 % chitosan. Improvement in the TM values of the composite films is due to the higher modulus of chitosan (450 MPa) as compared to PCL (220 MPa). These results clearly suggest that chitosan film acts as a reinforcement agent in composite films. TM
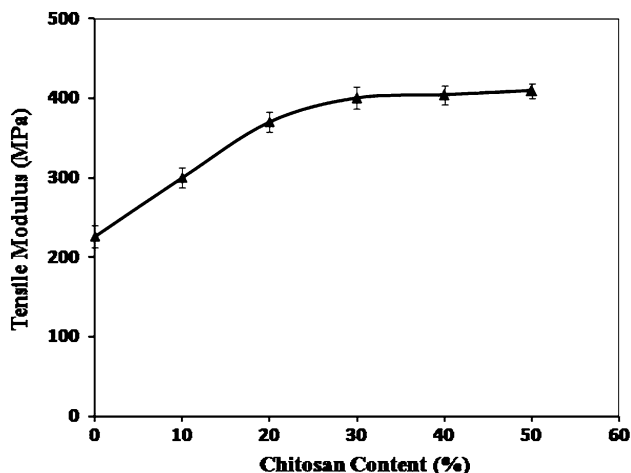

Fig. 2 Tensile modulus of the composite films against chitosan-based film content in PCL

values reached a plateau at 50 % chitosan content in the composite films. There was no significant improvement ($p > 0.05$) in the TM values after 40 % chitosan content, for similar reasons as mentioned above, relatively due to the strong hydrophilic nature of chitosan as compared to PC, leading to a poor interfacial adhesion.

Elongation at Break (Eb)

The Eb values of PCL and chitosan films were measured. The Eb values of chitosan and PCL films were found to be 8 and 70 %, respectively. Figure 3 shows the effect of chitosan content on the Eb of PCL-based composite films. A continuous significant decrease ($p \leq 0.05$) of Eb values was observed with an increase of chitosan content (10–50 %) in the composite films. It was observed that for the addition of 10 % chitosan in PCL matrix, Eb value of the composite decreased to 23 %. But for 50 % chitosan content in composite, Eb value reached to 7.9 % which indicated 90 % decrease of Eb values. This is attributable to low Eb values of chitosan films compared to PCL films. Moreover, all the chitosan containing specimens showed lower values of Eb than the matrix (PCL). At higher weight fraction of chitosan film, which acts as a reinforcing material, the composite tends to become somewhat more rigid. Here, chitosan is acting as a reinforcing agent in PCL-based films and consequently, higher amounts of chitosan can make the composites stiffer. The decreased Eb values may be related to the increased stiffness of the composite films by the addition of chitosan films.

Investigation of Failure Modes by Stress–Strain Curves

To investigate the fracture modes of the composite films, stress–strain curves were studied. The strain–stress curves for PCL, chitosan and composite films are presented in Fig. 4. PCL exhibited extensive strain up to 40 mm which indicated very high elongation (70 %). On the other hand, chitosan film showed sharp peak corresponds rigid and brittle nature. Just after 2 mm of strain, film breakage occurred and indicated very low elongation (8 %). The composite film exhibited two peaks. First peak represented chitosan and second one was for PCL. Here 20 % chitosan film reinforced PCL-based composites were investigated. The composite film had moderate elongation values (32 %), as discussed in Fig. 3. The maximum stress (41N) was observed at 2 mm strain and then chitosan film fractured. Then the composite again reached to 26N at 5 mm of strain, finally arrive at 20 mm of strain. From this investigation, this is clearly reveled that chitosan film was successfully reinforced with PCL films during compression molding. Mechanical bond formed between chitosan film and PCL films and thus formed a strong interface. If the
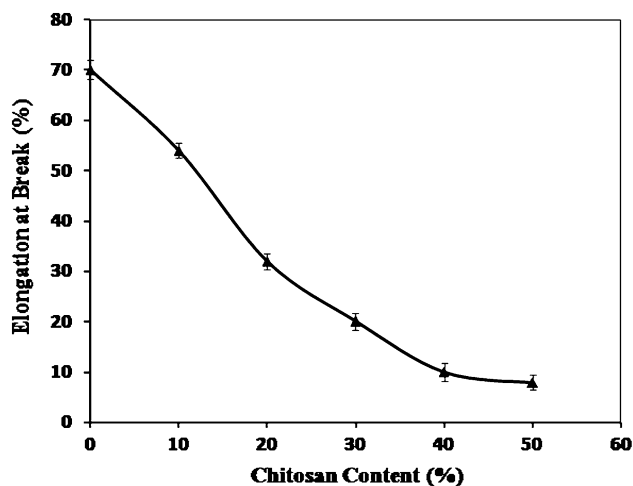
Fig. 3 Elongation at break of the composite films against chitosan-based film content in PCL

two types of films (chitosan and PCL) were not bound together then the composite film reached to the strain of PCL (40 %). But here, it is clear that the composite film fractured much earlier than PCL film. The results are in accordance with the general rules of polymeric materials. It is mentioned that polymers are classified into three types according to the type of stress–strain curves. In brittle polymers such as polystyrene, the stress–strain curves are linear up to the fracture point. Tough polymers such as polyethylene exhibit a yield point followed by extensive elongation at almost constant stress. The third type of stress–strain curve is exhibited by elastomers such as polyurethane, in which a nonlinear curve up to break point, and the elongation percentage may be of the order of several hundred percent [27].
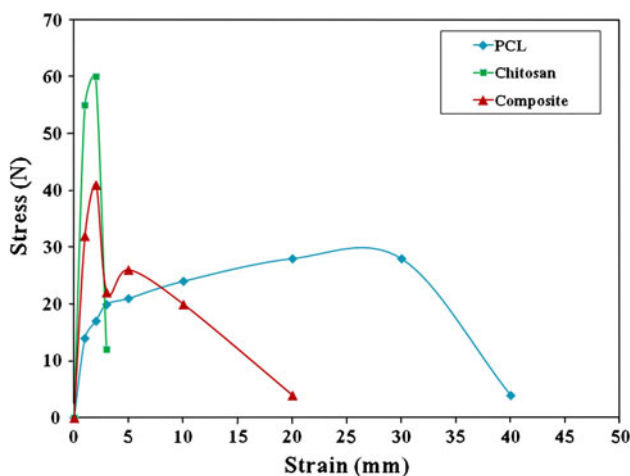
Water Uptake of the Composite

Water uptake of PCL, chitosan and composite (chitosan film reinforced PCL-based) was investigated up to 144 h (6 days). The results are shown in Fig. 5. PCL is strongly hydrophobic in nature and after 24 h of immersion of PCL films in water, the water uptake value was found to be only 0.2 %. Further increase of immersion time of PCL films, there were no changes in water uptake values. On the other hand, chitosan films were readily soluble in water because of the presence on acetic acid. Chitosan was dissolved in 2 % acetic acid solution for film formation (discussed in "Materials and Methods" section). To make insoluble films using chitosan films, PCL was coated on both sides by the film by compression molding. The water uptake of the composite was found to be 1, 2, 2.5, 2.6, 2.9 and 3 % for 24, 48, 72, 96, 120 and 144 h of soaking time, respectively. It is clear that water uptake values seemed to reach a plateau after 48 h of the soaking time. Since PCL is strongly hydrophobic in nature and the upper and lower layers of the composite were composed of PCL, chitosan absorbed water through the cutting edges. For this reason, the water uptake of the composite was so low to a value.

Water Vapor Permeability (WVP)

The WVP of PCL and chitosan films was found to be 1.54 and 4.74 g mm/m^2 day kPa, respectively. The effect of chitosan content on WVP of composite materials is shown in Table 1. It is clear that the values of WVP increase significantly ($p \leq 0.05$) with increasing chitosan content in the composite. For 10, 20, 30, 40 and 50 % chitosan
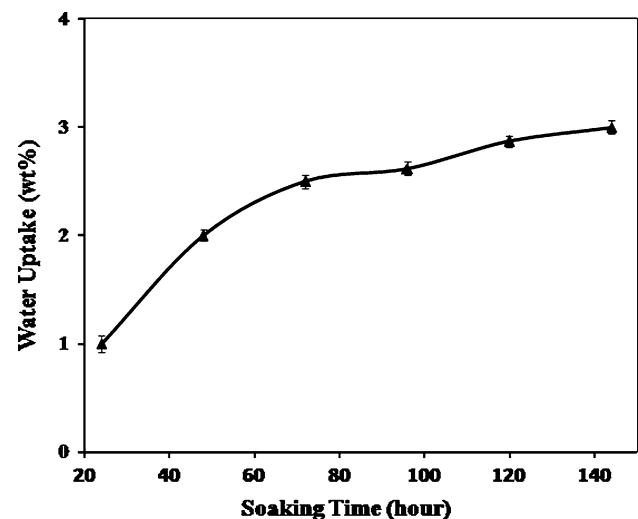

Fig. 4 Stress-strain curve of PCL, chitosan and composite (20 % chitosan)

Fig. 5 Water uptake of the composite films

Table 1 Water vapor permeability (WVP) of PCL, chitosan and chitosan reinforced composite films

Material	WVP (g mm/m² day kPa)
PCL film	1.54 ± 0.04[a]
Chitosan film	4.74 ± 0.05[g]
Composite film (10 % chitosan content)	1.82 ± 0.04[b]
Composite film (20 % chitosan content)	2.08 ± 0.01[c]
Composite film (30 % chitosan content)	2.37 ± 0.02[d]
Composite film (40 % chitosan content)	2.58 ± 0.06[e]
Composite film (50 % chitosan content)	2.65 ± 0.10[f]

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

content, the WVP values of the composites were found to be 1.82, 2.08, 2.37, 2.58 and 2.65 g mm/m² day kPa, respectively. The WVP values were in between the values of PCL and chitosan films. At 50 % chitosan content composites, the WVP value was improved by 72 % compared to PCL films. These results are mainly due to the higher WVP values of chitosan (4.74 g mm/m² day kPa) as compared to PCL (1.54 g mm/m² day kPa). Owing to the large amount of hydrogen bonds, most of the biopolymeric films are strongly hydrophilic, that is responsible for poor barriers to water vapor [28–30]. 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 (one chitosan film was sandwiched by two PCL films). The upper layer is PCL, which protects water vapor penetration and thus there was an improvement in the water vapor barrier properties. Azeredo et al. [31] reported that the water vapor barrier properties of chitosan films were improved significantly by the addition of cellulose nanofibers. They mentioned that a nanocomposite film with 15 % cellulose nanofibers and plasticized with 18 % glycerol was comparable to synthetic polymers in terms of strength and stiffness. In this investigation, composites were made by reinforcing one chitosan film by two PCL films. In composites, the middle layer is chitosan film and was covered by PCL films which had lower WVP values. As a result, the composites showed better water vapor barrier than chitosan films.

Oxygen Transmission Rate (OTR)

The OTR is one of the most important parameters that affect the food quality and shelf life. The OTR is defined as the quantity of oxygen gas passing through a unit area of the parallel surface of a film per unit time under predefined oxygen partial pressure, temperature, and relative humidity. Table 2 represents the OTR of PCL, chitosan films and composite (50 % chitosan content). The OTR values of

PCL, chitosan and composite (50 % chitosan content) films were 175, 3.17 and 8.18 cc/m² day respectively. It is clear that the OTR values of the PCL films are much higher than chitosan and composite films. The composite films showed to some extent higher OTR than that of chitosan films. A significant decrease of OTR was observed for PCL-based composites compared to control PCL films. It was already reported that synthetic polymeric films (PCL, polypropylene, polyethylene, etc.) have higher OTR than biopolymers (chitosan, cellulose derivatives, milk proteins, alginate, etc.) [31]. Indeed, due to the presence of hydroxyl groups, there are large amounts of hydrogen bonds in biopolymer films, which makes them hydrophilic. Thus, these hydrogen bonds make them excellent barriers to non-polar substances such as oxygen [28–32].

Thermal Properties of the Composite

Thermal properties (onset of melting, glass point and offset of melting temperatures) of PCL film and composite were evaluated by using the thermo-mechanical analyzer (TMA). The results are presented in Table 3. The onset, glass point and offset of melting temperatures of PCL were found to be 59, 63 and 65 °C, respectively. But composite containing 50 % chitosan showed 62, 66 and 69 °C, respectively for onset, glass point and offset of melting temperatures. These results showed that composites performed to some extent better thermal stability than PCL. It seems that due to the reinforcement of chitosan film inside PCL, the onset, glass point and offset of meting temperatures of composites improved. This is because of higher temperature resistant properties of chitosan films. It is to be noted here that chitosan film did not show onset, glass point and offset values. The TMA was run up to 500 °C and after 300 °C, chitosan film started to burn and turned to ash at 500 °C. Up to 100 °C, chitosan film was found almost intact. So, composites had little bit higher thermal properties over the matrix material PCL. The justification of the minor improvement in thermal properties of composites can be explained on the basis of the principles of TMA machine. In TMA, there is a quartz probe (niddle type) which penetrates inside the polymer with the rise of temperature. For PCL films, the probe of TMA started to penetrate at 59 °C (onset of melting), but for composite, it penetrated at 62 °C. The reason of this enhancement is mainly for the improvement of the stiffness of the material (composite). The composite became hard and strong because of the reinforcement of chitosan films in PCL.

Scanning Electron Microscopic Analysis (SEM)

Figure 6 represented the SEM image of the cross-section of the composite (PCL/chitosan/PCL).

Table 2 Oxygen transmission rate (OTR) of PCL, chitosan and composite film

Material	PCL film	Chitosan film	Composite film
OTR (cc/m^2 day)	175.00 ± 0.21^c	3.17 ± 0.25^a	8.18 ± 0.13^b

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

Table 3 Thermal properties of PCL, chitosan and composite film

Material	Melting temperature (°C)		
	Onset	Glass point	Offset
PCL	59	63	65
Chitosan	Nd	Nd	Nd
Composite (PCL + 50 % Chitosan)	62	66	69

Nd non detectable
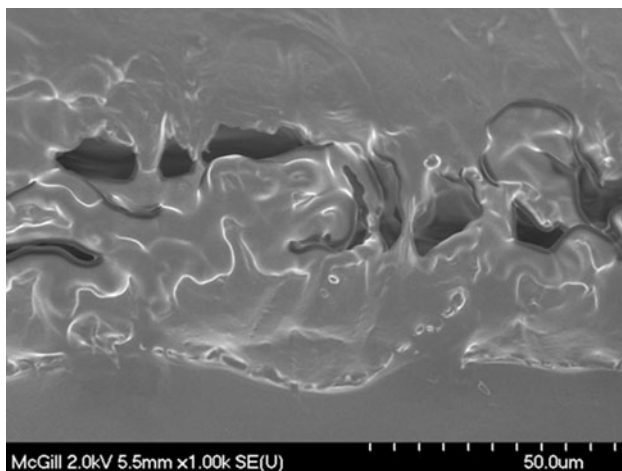
Fig. 6 Scanning electron microscopic (SEM) image of the interface of the composite

The cross-section corresponded to the interface of the composite. In the interface, some voids were evident. Voids were occurred between PCL and chitosan films. The composite was a tri-layer type. One chitosan film (middle) was reinforced with two PCL films (top and bottom). These films were clearly apparent in the image. The top and bottom parts were looked smooth and homogenous which indicated PCL films. The middle layer corresponded chitosan film. At the upper portion of chitosan film, few voids occurred which might be attributed from the strong hydrophilic nature of chitosan and hydrophobic PCL. Some voids and holes were reported for chitosan and PCL blended films [33].

Conclusions

Biodegradable chitosan films were prepared by solution casting. On the other hand, PCL films were prepared by compression molding. Then chitosan film reinforced PCL-based biodegradable composites were prepared successfully by compression molding. Mechanical (tensile strength, tensile modulus and elongation at break), thermal, water vapor and oxygen barrier properties of the films were measured. Chitosan content in the composite was varied from 10 to 50 % by weight. Chitosan film was sandwiched with PCL matrix, in order to investigate the effect of chitosan content on the mechanical, degradation, barrier and interfacial properties of PCL-based biodegradable films. It was found that chitosan contributed to the improvement of mechanical properties of the composites. With the increase of chitosan content, there was a significant improvement in the tensile properties and water vapor barrier properties. Similarly OTR of the composite films was decreased drastically as compared to PCL, which indicates enhanced oxygen barrier properties. SEM analysis of composite interface morphology also provided justification of the improved properties obtained by chitosan incorporation in PCL-based composite films and leading to a very stable interface. From all these supported measurements, chitosan was found to be a very good reinforcing agent in PCL-based biodegradable composite films for packaging applications.

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