

Mechanical and Barrier Properties of Nanocrystalline Cellulose Reinforced Poly(caprolactone) Composites: Effect of Gamma Radiation

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ABSTRACT: Nanocrystalline cellulose (NCC) reinforced poly(caprolactone) (PCL) composites were prepared by compression molding. The NCC content varied from 2 to 10% by weight. NCC played a significant role in improving the mechanical properties of PCL. The addition of 5 wt % NCC caused a 62% improvement of the tensile strength (TS) value of PCL films. Similarly, tensile modulus (TM) values were also improved by NCC reinforcement but elongation at break (Eb) values decreased monotonically with NCC content. The water vapor permeability (WVP) of PCL was 1.51 g·mm/m²·day·kPa, whereas PCL films containing 5 wt % NCC showed a WVP of 1.22 g·mm/m²·day·kPa. The oxygen transmission rate (OTR) and carbon dioxide transmission rate (CO₂TR) of PCL decreased by 19 and 17%, respectively, with 5 wt % NCC incorporation. It was found that the mechanical and barrier properties of both PCL and PCL-NCC composites further improved with 10 kGy gamma irradiation treatment. The combination of NCC and radiation significantly increased the TS, TM, and Eb (by 156, 123, and 80%, respectively, compared to untreated PCL). The WVP, OTR, and CO₂TR decreased by 25–35% with respect to untreated PCL. The surface and interface morphologies of the PCL-NCC composites were studied by scanning electron microscopy and suggested homogeneous distribution of NCC within the PCL matrix.
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INTRODUCTION

In recent years, nanotechnology has gained much attention for its vital pioneering role in manipulating materials at the atomic and molecular levels to dramatically alter the product properties. Materials reduced to the nanometric scale display significantly different properties compared to what they display at the macroscale or microscales. Because of their unique properties, nanomaterials are widely used in a variety of applications. In the packaging sectors, nanomaterials are in great demand as reinforcing agents to improve the thermomechanical and barrier properties of packaging films. Nanomaterials may also be used in packaging films to improve controlled release properties by better encapsulation of bioactive compounds. Small amounts of nanoparticles may thus play a vital role in developing biodegradable synthetic thermoplastic polymers.^{1–5} For example, silica-based nanoparticles-reinforced polymeric nanocomposite films for packaging performed excellent thermomechanical and barrier properties.^{6,7}

Synthetic polymers such as polyethylene and polypropylene are widely used as packaging materials because of their unique properties such as good thermomechanical and barrier properties. Packaging films made of these polymers are also very inexpensive. However, these polymers are not biodegradable. Research is, therefore, in progress to develop alternative environmentally friendly packaging materials. Biodegradable polymers under consideration include poly(caprolactone) (PCL), poly(lactic acid), poly(glycolic acid), and other biopolymers including chitosan, alginate, cellulosic materials. While these materials are environmentally friendly, their films have poor thermomechanical and barrier properties compared to the commercial packaging currently in use. Therefore, many studies are now aiming to develop biodegradable films having physicochemical attributes approaching those of nonbiodegradable polymers.^{8,9}

In this investigation, PCL was chosen as the biodegradable matrix material. PCL is a thermoplastic aliphatic polyester

produced by chemical synthesis from crude oil via the ring opening polymerization of caprolactone monomer. It is partly crystalline with a glass transition temperature of about -60°C , a low melting point ($58-64^{\circ}\text{C}$), and low melt viscosity, making it easy to process. The main commercial application of PCL is in the manufacture of biodegradable bottles and compostable bags.¹⁰⁻¹²

Nanocrystalline cellulose (NCC) is an interesting nanomaterial for the production of cheap, lightweight, and very strong nanocomposites. NCC is obtained from native cellulose sources and is composed of nanometer-sized rod like particles. The NCC used in this study is extracted from bleached softwood kraft pulp by controlled acid hydrolysis. Wood cellulose nanocrystals have cross-sectional dimensions of 6–7 nm and lengths ranging from 80 to 100 nm. NCC is expected to show high stiffness since the Young's (elastic) modulus along the axis of the cellulose nanocrystals is 137 GPa or greater.¹³⁻¹⁵ The tensile strength (TS) of the crystal structure was assessed by modeling to be approximately 7.5–7.7 GPa.¹⁶ It is anticipated that NCC nanocomposites may provide value-added materials with superior performance and extensive applications for the next generation biodegradable materials.¹⁷ Cellulose nanocrystals are expected to be excellent reinforcing agent for thermoplastic polymers because of their outstanding mechanical properties and large aspect ratio. Generally, dried NCC tends to aggregate due to its small size, high surface energy, and strong intrinsic van der Waals forces. In this investigation, PCL-NCC composite films were prepared by melt blending process. Melt blending is a simple technique and is widely used by researchers as it can be performed in the laboratory in a manner similar to industrial practice.¹⁷⁻²⁰

Gamma radiation is widely used to modify the structure and properties of polymers, and can be used to tailor the performance of either bulk materials or surfaces. Over the past few decades, there has been a continuous and significant growth in the development and application of radiation techniques including gamma radiation. Gamma radiation is a type of ionizing radiation. Irradiation of polymers with high-energy gamma rays leads to the formation of very reactive intermediates in the forms of excited states, ions, and free radicals. These intermediates are almost instantaneously consumed in several reaction pathways which ultimately produce oxidize products, grafts, crosslinking, and scission of main or side chains (degradation). The relative extent of these transformations depend on the nature of the polymer and the treatment condition during and after irradiation, and close control of these factors makes possible the modification of polymers by radiation processing. The use of gamma radiation offers several advantages, such as continuous operation, minimum time requirement, less atmospheric pollution, and curing at ambient temperatures. Radiation induced processes also have many advantages over other conventional methods. No catalysts or additives are required to initiate the reaction, as absorption of radiation energy by the polymer backbone generally initiates a free radical process. In addition, the radiation dose rate can be easily varied making control of reaction easier and precise. Finally, radiation processing is temperature independent and is therefore considered a zero activation energy process.²¹⁻²⁴

The objective of this study was to develop NCC-reinforced PCL composite films for food packaging by melt blending process. Mechanical (strength, modulus, and elongation), barrier [water vapor permeability, oxygen and carbon dioxide transmission rates (CO_2TR)], and morphological [scanning electron microscope (SEM)] properties of the composite films were evaluated and compared with neat PCL films. Both PCL and PCL-NCC composites were exposed to gamma radiation to evaluate the effect of irradiation on the mechanical and barrier properties of PCL-NCC composites.

MATERIALS AND METHODS

Materials

PCL, granular form, molecular weight 70,000–80,000, was purchased from Sigma-Aldrich Canada (Oakville, ON, Canada). NCC was supplied by FPInnovations (Pointe-Claire, QC, Canada) and was prepared in their pilot scale NCC reactor. The NCC was extracted from commercial bleached softwood kraft pulp.

Preparation of PCL and PCL-NCC Composite Films by Compression Molding

PCL films were prepared from PCL granules by compression molding machine (Carvar, IN, Model 3912) at 110°C under a consolidation pressure of 2 tons for 1 min. The mould containing the PCL film was rapidly cooled in an ice bath for 2 min. The PCL film was then taken out from the mould and kept in a desiccator prior to characterization. NCC reinforced PCL composites were prepared by melt blending using the rig of the in-house melting mixer. PCL granules were melted at 110°C and mixed with NCC powder under continuous stirring for 10 min. The mixture was hot pressed in the same compression molding machine using the same parameters.

Film Thickness

Film thickness was measured using a Mitutoyo Digimatic Indicator (Type ID-110E, Mitutoyo Manufacturing Company, Tokyo, Japan) at five random positions around the film.

Mechanical Properties of the Films

The TS, tensile modulus (TM), and elongation at break (Eb%) of PCL and PCL-NCC composite films were measured with a Universal Tensile Machine (Tinius-Olsen, 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): $60 \times 15 \times 0.05 \text{ mm}^3$.

WVP of Films

The WVP tests were conducted gravimetrically using an ASTM procedure.⁵ Films were mechanically sealed onto vapometer cells (No. 68-1, Thwing-Albert Instrument Company, West Berlin, NJ) containing 30 g of anhydrous calcium chloride [0% relative humidity (RH)]. The cells were initially weighed and placed in a Shellab 9010L controlled humidity chamber (Sheldon Manufacturing, 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% mass gain. Changes in the weight of the cell were recorded to the nearest 10^{-4} g . WVP was calculated according to the combined Fick and Henry laws for gas diffusion through coatings and films, according to the equation: $\text{WVP} (\text{g}\cdot\text{mm}\cdot\text{m}^{-2}\cdot\text{day}^{-1}\cdot\text{kPa}^{-1}) = \Delta w / \lambda A \Delta P$,

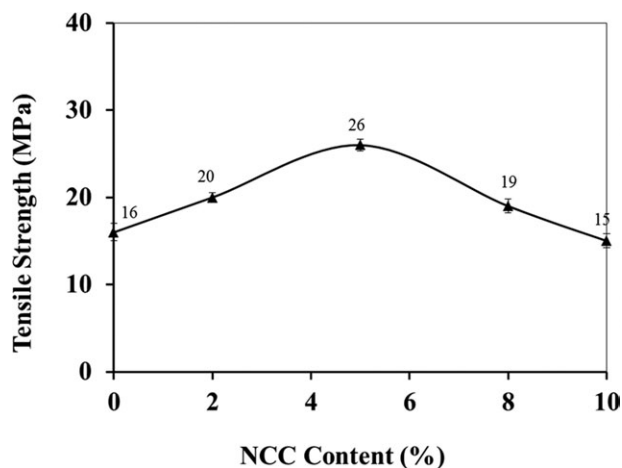


Figure 1. Tensile strength of PCL-NCC composite films as a function of NCC content.

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 ($31.67 \times 10^{-4} \text{ m}^2$), and ΔP is the differential vapor pressure of water through the film (3.282 kPa at 25°C).

Measurement of Oxygen Transmission Rate (OTR)

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 RH.¹² The OTR was measured using an OX-TRAN® 1/50 (MOCON®, MN) machine. During all experiments, temperature and RH were held at 23°C and 0% RH. The experiments were done in duplicate and the samples (dimensions: 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. Readings were recorded as $\text{mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$.

Carbon Dioxide Transmission Rate (CO₂TR)

The CO₂TR of films was measured using a Mocon Permatran-C™ 4/41 (MOCON®, MN). All analyses were carried out under atmospheric conditions at 23°C and 0% RH. Readings were recorded as $\text{mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$.

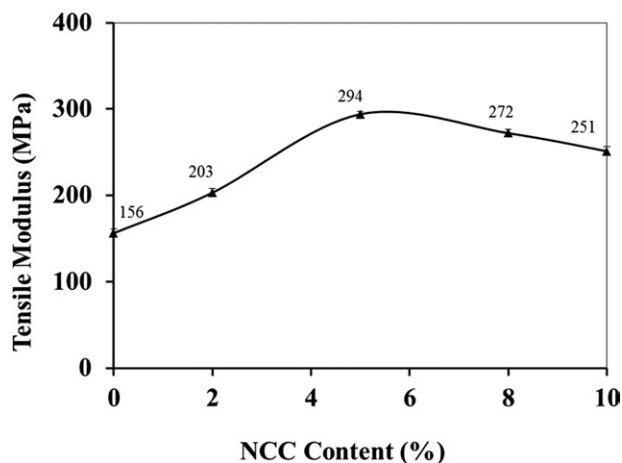


Figure 2. Tensile modulus of PCL-NCC composite films as a function of NCC content.

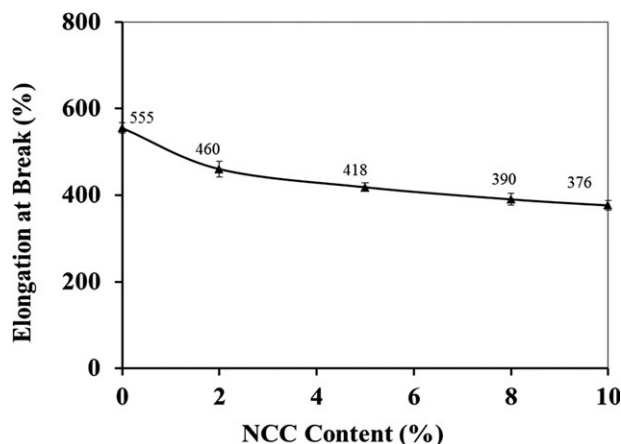


Figure 3. Elongation at break PCL-NCC composite films as a function of NCC content.

Scanning Electron Microscope (SEM) Analysis

Film samples ($5 \times 5 \text{ mm}^2$) were deposited on an aluminum holder and sputtered with gold–platinum (coating thickness, 150–180 Å) in a Hummer IV sputter coater. SEM micrographs were taken at room temperature with a Hitachi S-4700 FEG-SEM (Hitachi Canada, Mississauga, ON, Canada).

Irradiation of Films

Film samples to be irradiated were placed in polyethylene bags. Irradiation of films was conducted with γ -rays generated from a ^{60}Co source at room temperature, at a dose rate of $17.878 \text{ kGy h}^{-1}$ in an Underwater Calibrator-15A Research Irradiator (Nordion, Kanata, ON, Canada).

Statistical Analysis

For each measurement, five replicate samples were tested. Analysis of variance and Duncan’s multiple-range tests were used to perform statistical analysis on all results, using the PASW Statistics Base 18.0 software (SPSS, Chicago, IL). Differences between means were considered to be significant when $P \leq 0.05$.

RESULTS AND DISCUSSION

Mechanical Properties of NCC-Reinforced PCL Composite Films

The mechanical properties of PCL films and PCL-NCC composite films were evaluated and the results are presented in Figures 1–3. The thickness of the PCL films and composites was around $50 \mu\text{m}$. The TS of the PCL films was found to be 16 MPa. Addition of NCC significantly ($P \leq 0.05$) improved the TS values. The NCC content in the PCL-NCC composites varied from 2 to 10% by weight. Figure 1 shows the effect of NCC addition on PCL films. With 2, 5, 8, and 10% by weight incorporation of NCC, the TS values were 20, 26, 19, and 15 MPa, respectively. The highest TS value was observed at 5 wt % NCC content which was a 62% improvement over the original PCL films. The significant improvement in strength PCL occurred due to the very high strength of cellulose microfibrils and hence the added NCC.²⁰ Azeredo et al.¹⁷ mentioned that the strength of edible mango puree films was significantly improved by the addition of cellulose nanofibers. Lee et al. observed that the tensile and thermal properties of polyvinyl alcohol-based composite

films were significantly improved with increase NCC loading.²⁵ In another study, Khan et al. reported that NCC improved the thermomechanical properties of methylcellulose-based biodegradable films.⁵

Similarly, the TM of PCL films was also improved by the incorporation of NCC. Figure 2 shows the effect of NCC content on the TM values of the neat PCL films. The TM of PCL film was 156 MPa. At 2, 5, 8, and 10% by weight NCC content, the TM values of the composites were found to be 203, 294, 272, and 251 MPa, respectively, which are significant increase ($P \leq 0.05$). At 5 wt % NCC incorporation, the PCL films showed an 88% increase in TM. Addition of NCC thus improved the stiffness and strength of PCL films. At higher NCC contents, the material tends to become somewhat more brittle. This is a common observation in both nanocomposites as well as conventional composite materials. The increased TM values are related to the increased stiffness of the composite films by the addition of NCC.²⁶ As a result, a decrease in TM values was observed above 5 wt % addition of NCC.

The Eb of PCL was observed to be 555%. Figure 3 illustrates the effect of NCC reinforcement on the Eb of PCL films. With the incorporation of NCC, the Eb values of PCL films decreased monotonically. The Eb decreased to 418% at 5 wt % incorporation of NCC. Generally, with increased loading of reinforcing agent, the strength and modulus of composites increase but the elongation at break is decreased.⁵ From this investigation, it is clear that addition of NCC caused a significant increase in both strength and modulus. The highest strength and modulus were observed at 5 wt % NCC reinforcement in PCL, above which both strength and modulus decreased. The monotonic decrease in the elasticity (Eb) of PCL films with increasing NCC loading confirms that NCC acts as a reinforcing agent in PCL. Thus, the solid-like behaviour of PCL appears to become more prominent with increasing NCC content. Similar results have been obtained by researchers who reported a decreased Eb with increasing addition of cellulose nanofibers in polymer films.^{27,28}

WVP of PCL and PCL-NCC Composite Films

Owing to high numbers of hydroxyl bonds present in their structure, most biodegradable polymeric films are hydrophilic, with the result that they are poor barriers to water vapor.²⁹ The WVP of PCL film was found to be $1.51 \text{ g}\cdot\text{mm}\cdot\text{m}^{-2}\cdot\text{day}^{-1}\cdot\text{kPa}^{-1}$. Figure 4 shows the effect of NCC on the WVP of the PCL-NCC films. The presence of NCC in the PCL composites is responsible for lower WVP values compared to control PCL films, the WVP values decreasing monotonically with increasing NCC content. The WVP values of 2, 5, 8, and 10% NCC by weight PCL composite films were 1.42, 1.22, 1.12, and 1.01 $\text{g}\cdot\text{mm}\cdot\text{m}^{-2}\cdot\text{day}^{-1}\cdot\text{kPa}^{-1}$, respectively. At 5 wt % NCC content, the WVP of PCL films decreased by 19%. The presence of NCC nanocrystals is thought to increase the tortuosity in the PCL composite films, leading to slower diffusion processes and hence, to lower WVP.¹² The barrier properties are also enhanced if the reinforcing filler is less permeable and is well-dispersed in the matrix.³⁰ In the present study, the interactions of NCC with PCL likely enhanced the water vapor barrier properties.⁵ The WVP values of the PCL-NCC composites indicated a significant

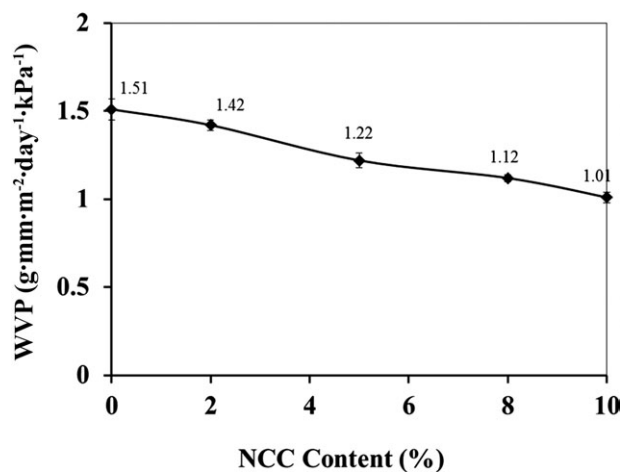


Figure 4. Water vapor permeability (WVP) PCL-NCC composite films as a function of NCC content.

improvement in water vapor barrier properties over those of the native PCL films.

OTR of PCL and PCL-NCC Composite Films

Modified atmosphere packaging has gained considerable popularity over the last decades as a nonthermal method of food preservation. The proper combination of gases (carbon dioxide, nitrogen, and oxygen) in the headspace of food packs results in suppression of the microbial flora of perishable foods that developed under aerobic conditions and improves retention of their olfactory and visual properties. Hence, the OTR and CO_2TR are equally important and were both measured.

The transfer of oxygen from the environment to packaged food has an important effect on food quality and shelf life. The OTR of the packaging is very important since oxygen gas influence the rates of oxidation and respiration in the enclosed food, including fruits and vegetables. Oxygen causes food deterioration such as lipid and vitamin oxidation, leading to sensory and nutrient changes. Figure 5 represents the OTR of PCL and PCL-NCC composite films as a function of NCC content. It is clear that NCC-containing PCL composite films showed much lower OTR values than neat PCL films. The OTR value of the native PCL film was found to be $175 \text{ mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. Incorporation of 2, 5, 8, and 10% by weight NCC in PCL films decreased the OTR values to 160, 146, 136, and 121 $\text{mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$, respectively. A 5 wt % NCC reinforced PCL-based composites showed a 17% reduction of OTR. Synthetic polymers (PCL, polypropylene, polyethylene, etc.) generally have higher OTR values.^{31–34} Addition of NCC to PCL increased the polarity or hydrophilicity of the composite and thus made it a better barrier to non-polar substances such as oxygen.

CO_2TR of PCL and PCL-NCC Composite Films

The CO_2TR value of PCL film was found to be $1170 \text{ mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. The composite films containing 2, 5, 8, and 10 wt % NCC showed CO_2TR values of 1100, 960, 842, and 730 $\text{mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. Figure 6 represents the CO_2TR of PCL and PCL-NCC composite films. The NCC containing composite films showed significantly lower CO_2TR values than neat PCL films.

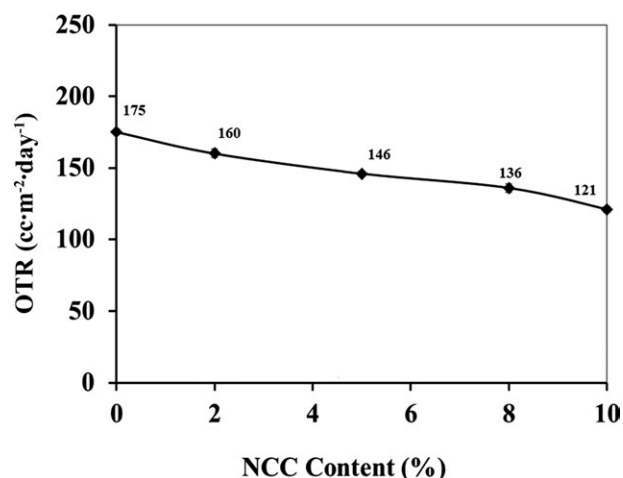


Figure 5. Oxygen transmission rate (OTR) PCL-NCC composite films as a function of NCC content.

Addition of 5 wt % NCC to PCL caused an 18% reduction in CO₂TR values. The CO₂TR of biopolymers tend to be very low because of their strong hydrophilic nature; the CO₂TR values of synthetic polymers are very much higher.³⁴ It is reported³⁵ that the CO₂TR of high-density polyethylene is 17,470 mL·m⁻²·day⁻¹. Synthetic aliphatic polymers are strongly hydrophobic and are therefore weaker barriers to nonpolar gases such as carbon dioxide. Thus, when NCC is added to PCL, the CO₂TR decreases because the composite becomes more hydrophilic in nature.

Effect of Gamma Radiation on PCL and PCL-NCC Composites

Gamma radiation is a very high frequency electromagnetic radiation that produces three types of reactive species when it interacts with polymeric materials such as PCL: ions, radicals, and peroxides. Ions are produced by the photoelectric effect, the Compton effect, and pair production.^{36,37} Radicals are produced on the main polymer chain by hydrogen and hydroxyl abstraction, and by the rupture of some carbon-carbon bonds (chain

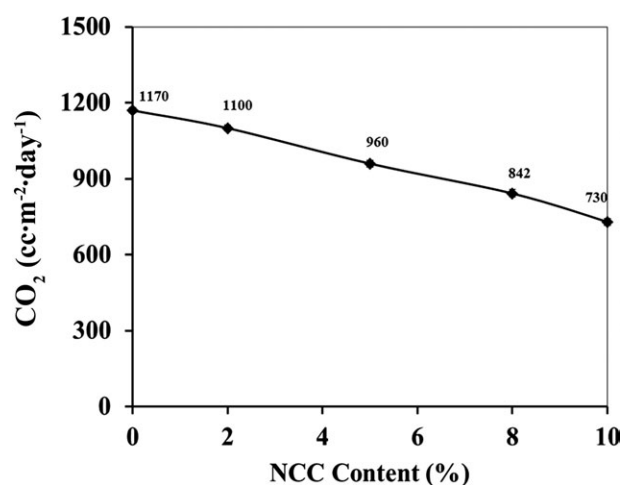


Figure 6. Carbon dioxide transmission rate (CO₂TR) of PCL-NCC composite films as a function of NCC content.

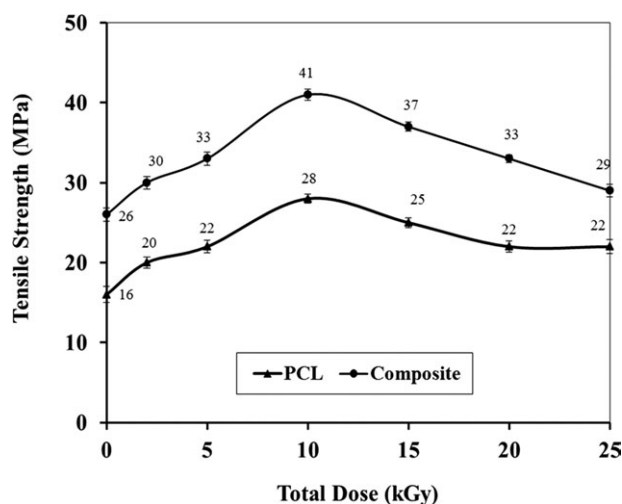


Figure 7. Effect of gamma radiation on the tensile strength of PCL and PCL-NCC (5 wt %) composite films.

scission).³⁶⁻³⁸ The radical species may then react with each other to produce cross-links in the polymer structure. Peroxide species are produced by a radical chain reaction process when polymers are irradiated in the presence of oxygen, which is the case for this investigation. PCL-diperoxides and PCL-hydroperoxides may, therefore, have formed in the polymer matrix. These peroxide species may then initiate crosslinking by decomposing to produce highly reactive free radicals which in turn react with polymer molecules to produce polymer radicals that combine randomly with one another to produce crosslinks.³⁹⁻⁴² PCL, therefore, may undergo crosslinking with gamma radiation and thus the mechanical and barrier properties may improve up to a certain dose. At higher doses of gamma radiation, PCL may undergo cleavage or scission as described above and thus show a decline in mechanical properties.^{43,44}

When cellulosic materials such as wood pulp or NCC are subjected to gamma radiation, radicals are produced on the cellulose chain by hydrogen and hydroxyl abstraction. Glycosidic bonds are also ruptured leading to a decrease of the cellulose chain length by random depolymerization. An increase in carbonyl groups content is also observed.⁴⁵ A correlation exists between the concentration of free radicals formed in irradiated pulp and irradiation dosage.⁴⁶ At lower doses (<10 kGy) cellulose chains undergo crosslinking⁴⁷ whereas at higher doses, degradation by chain scission predominates.⁴⁸ Thus, at 10 kGy radiation, we can expect to see minimal degradation and partial crosslinking of the NCC particles.

Neat PCL films and 5 wt % NCC-reinforced PCL composites were exposed to gamma radiation at doses ranging from 2 to 25 kGy. Their TS, TM, and Eb values were then measured. The results are presented in Figures 7-9. It was found that gamma radiation had a significant influence on the strength of PCL and PCL-NCC composites as depicted in Figure 7. The irradiated films had significantly improved TS values. At 10 kGy, the PCL films reached a TS value of 28 MPa which is 75% higher than the nonirradiated control sample. Above 10 kGy, the TS values decreased to 22 MPa at 25 kGy, which is still higher than the

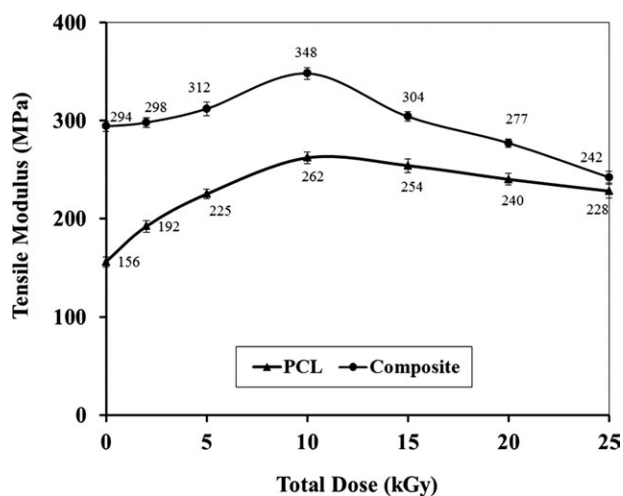


Figure 8. Effect of gamma radiation on the tensile modulus of PCL and PCL-NCC (5 wt %) composite films.

control sample. The TS of 5 wt % NCC-reinforced PCL was 26 MPa (Figure 1) but the strength of the films improved significantly after irradiation. At 10 kGy, the TS of the PCL-NCC composite films reached 41 MPa which is 58% higher than the control composite. It is clear that 10 kGy is the optimal radiation dose. Above 10 kGy, the decrease in film strength can be attributed to radiation degradation of PCL by molecular chain cleavage. The TS value of the 10 kGy-irradiated PCL film improved by 75%, whereas the irradiated PCL-NCC composite film improved by 58% over their respective controls. Most probably NCC nanocrystals partially hinder radiation-induced molecular crosslinking of PCL. But the major advantage was further improvement of the strength of the composites. The NCC (5 wt %) reinforcement and gamma irradiation (10 kGy) together significantly increased (156%) the strength of the PCL film.

Similarly, the TM values of PCL films improved significantly with exposure to irradiation. The results are depicted in Figure 8. The highest TM values for PCL and PCL-NCC were observed at 10 kGy. The TM value of neat untreated PCL (156 MPa) was significantly improved due to 5 wt % NCC reinforcement plus gamma radiation (10 kGy), reaching 348 MPa, which is a 123% improvement. Above 10 kGy, the TM values of PCL and NCC-PCL decreased slightly to around 230–240 MPa at 25 kGy. The irradiated PCL films showed 68% higher TM values at 10 kGy than the control films, whereas the PCL-NCC composites showed only 18% higher TM values than their counterpart control.

The effect of gamma radiation on Eb values of PCL and PCL-NCC composites is presented in Figure 9; the Eb values also improved with exposure to gamma radiation. This combination of property enhancement rarely occurs in composites. The maximum Eb values were obtained at 10 kGy radiation for both PCL (900%, a 62% improvement over unirradiated PCL) and 5 wt % NCC-reinforced PCL (998%, a 139% improvement over the unirradiated PCL-NCC composite). From this investigation, it is clear that gamma radiation plays a strong role in the

improvement of the mechanical properties of PCL films. The NCC-reinforced PCL composites also showed a trend of mechanical property enhancement but to a smaller extent than for neat PCL. The NCC nanocrystals may hinder the crosslinking of PCL molecules and thus weaken the tendency of irradiation to reduce the Eb.

The barrier properties of irradiated PCL and PCL-NCC composites were examined only at a radiation dose of 10 kGy, at which optimal mechanical properties were obtained. Gamma radiation (10 kGy) improved the water vapor barrier properties of PCL and PCL-NCC (5 wt %) composites. The WVP of neat PCL film decreased by 12% from 1.51 to 1.32 $\text{g}\cdot\text{mm}\cdot\text{m}^{-2}\cdot\text{day}^{-1}\cdot\text{kPa}^{-1}$ for irradiated PCL film. Similarly, the 5 wt % NCC-reinforced PCL composites showed a 19% lower WVP value due to 10 kGy irradiation. The WVP values for unirradiated and irradiated composites were 1.22 and 0.98 $\text{g}\cdot\text{mm}\cdot\text{m}^{-2}\cdot\text{day}^{-1}\cdot\text{kPa}^{-1}$, respectively. During irradiation of PCL and PCL-NCC composite films, crosslinking of PCL molecules likely occurred, reducing the PCL hydrophilicity and/or increasing the tortuosity (by increasing the polymer's amorphous character, see below) and thus improving its water vapor barrier properties.⁴⁹ It has been suggested^{15,37,49} that gamma radiation improves the water vapor barrier properties of polymeric films because of hydrogen bonds created by irradiation. In addition, the decrease in WVP of the PCL-NCC composite may be due to consumption of hydroxyl groups on the NCC surface through the formation of crosslinks with the PCL, resulting in lower hydrophilicity of the material.⁵ Our results are thus in accordance with the previous literature.

The OTR of the irradiated (10 kGy) PCL film was 224 $\text{mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ compared to 175 $\text{mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ for the untreated film as represented in Figure 5. A 28% increase of OTR was observed. During irradiation, the crosslinking process creates bigger and more subdivided polymer molecules, increasing the amorphous character of the partially crystalline PCL and thus allowing more oxygen to pass through.⁴¹ Conversely, the OTR of the irradiated (10 kGy) PCL-NCC composite (5 wt % NCC)

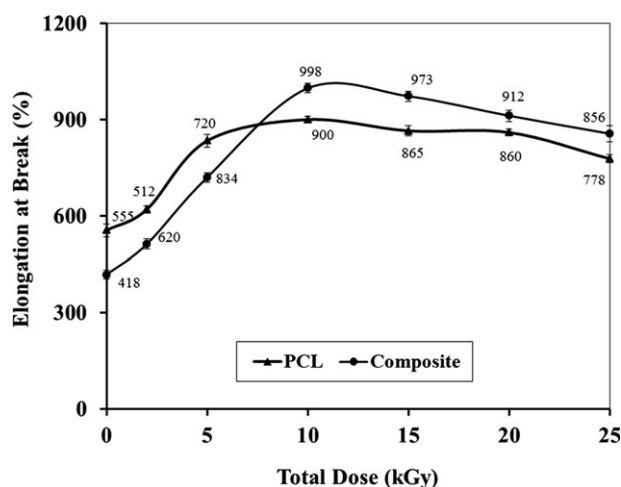


Figure 9. Effect of gamma radiation on the Eb of PCL and PCL-NCC (5 wt %) composite films.

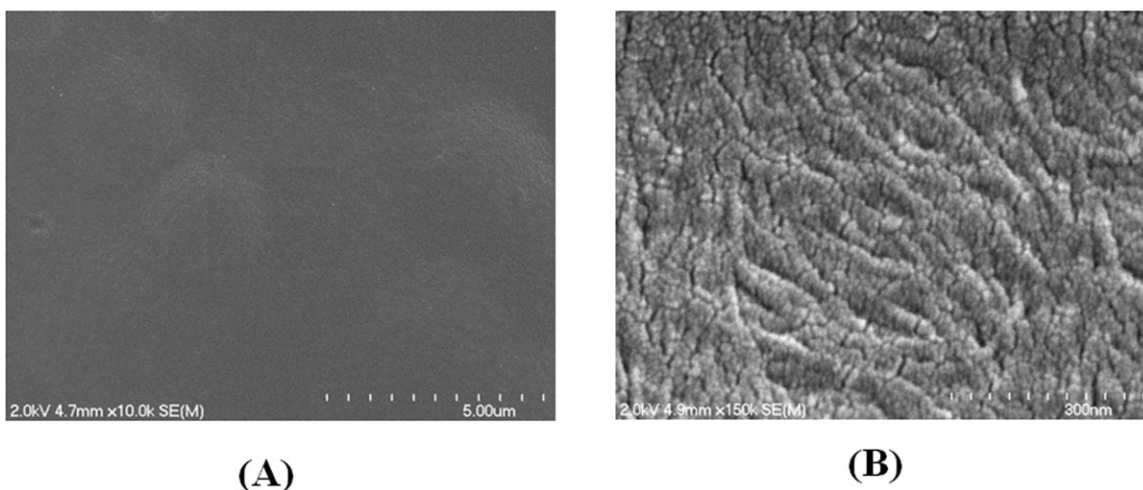


Figure 10. SEM images of the surface of (A) PCL and (B) NCC films.

decreased to $118 \text{ mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ from $146 \text{ mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ for the control composite.

The CO_2TR of PCL-NCC composite films as a function of NCC content is already explained in Figure 6. The CO_2TR of irradiated PCL was $1440 \text{ mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$, which is 23% higher than the control PCL films. The CO_2TR of the 5 wt % NCC-reinforced composite was $960 \text{ mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$, the CO_2TR of the irradiated (10 kGy) composite decreased by 12% to $849 \text{ mL}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. Both oxygen and carbon dioxide are nonpolar in nature but PCL is polar, hindering passage of these gases through the films. PCL is partially crystalline,^{8–10} the crystalline portions also hinder gas diffusion. Active sites can form in PCL during gamma radiation and chain scission may occur. During irradiation structural changes such as crosslinking occur in PCL as a result of which its crystallinity may decrease and its amorphous nature increase,⁴⁹ facilitating the passage of oxygen and carbon dioxide through the irradiated PCL. Most probably, the NCC hindered the radiation-induced polymer crosslinking, thereby allowing the PCL to retain more of its crystalline character; other radiation-induced interactions of

NCC and PCL may have also increased the crystallinity, decreasing the OTR.

Surface and Interface Morphologies of the Composite Films

The SEM images are shown in Figure 10. The surfaces of pure PCL (A) and NCC (B) films were investigated by SEM. The surface of the PCL film (A) appears quite homogeneous and smooth. Because the PCL films were prepared by compression molding, some irregularities appeared at the surface; this is caused by the release films used during hot pressing of PCL granules. Conversely, NCC films were made by casting from a 1 wt % aqueous suspension. The films were very brittle and it was difficult to measure their mechanical and barrier properties. The nanocrystals appear rod-like. Similar SEM images of nanocellulose have been reported.^{5,15,20,50}

Figure 11 shows SEM images of the (A) surface and (B) interface (fracture surface) of 5 wt % NCC-reinforced PCL composites. At the surface and interface, NCC particles were not visible. Due to pressing at high temperature (110°C), NCC particles penetrated inside the PCL matrix, to which might be

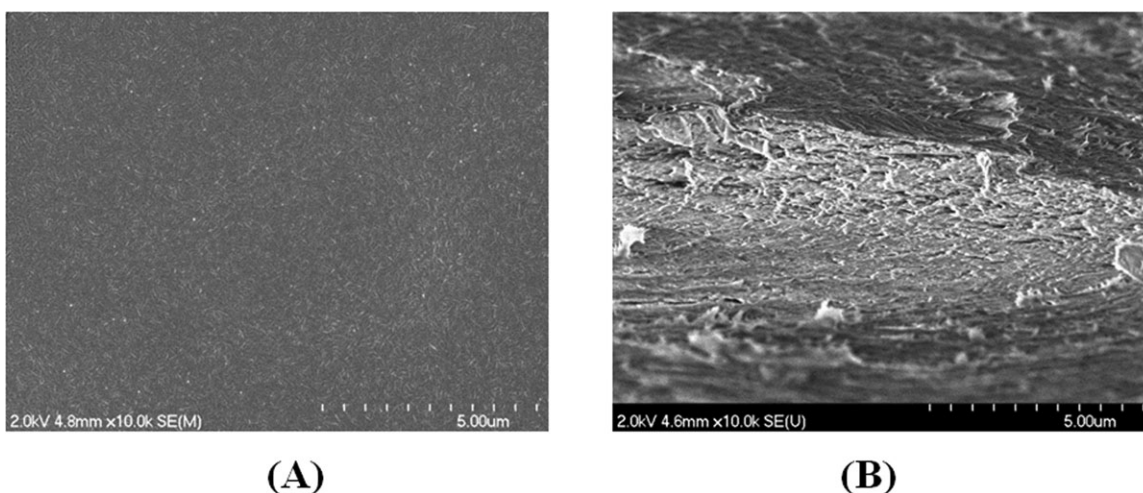


Figure 11. SEM images of the (A) surface and (B) interface of PCL-NCC (5 wt %) composite films.

attributed the smooth featureless composite surface, indicating homogeneous mixing of the NCC with PCL. However, it is possible that the white bubble-like spots at the surface of the film may be NCC. At the interface (fracture surface) of the composites, it is also difficult to see the nanocrystals of NCC. During melt blending of PCL with NCC, all the nanocrystals of NCC were submerged in the PCL matrix and the quantity was not only 5 wt %. Moreover, PCL is a thermoplastic type polymer which can cover or coat the surface of NCC particles. This might explain why NCC does not appear in SEM images of PCL-NCC composites.

CONCLUSION

NCC was found to be an excellent reinforcing agent for the thermoplastic biodegradable polymer PCL. The TS, TM, and Eb of PCL were significantly improved by the incorporation of small quantities of NCC. An addition of 5 wt % NCC caused a 62% improvement of strength of PCL films. The WVP, OTR, and CO₂TR of the PCL-NCC composites were significantly reduced compared to PCL, indicating better barrier properties of the composites. The prepared composite films are viable for use in modified atmospheric packaging applications. The effects of gamma radiation on PCL films and NCC containing PCL films were studied. It was found that irradiated films gained further mechanical and barrier properties over the counterpart control counterpart samples (TS, TM, and Eb values increased, whereas WVP, OTR, and CO₂TR all decreased). This investigation opens the door to new research for modified atmospheric packaging.

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