

## Mechanical and Barrier Properties of Carbon Nanotube Reinforced PCL-Based Composite Films: Effect of Gamma Radiation

Ruhul A. Khan,<sup>1</sup> Dominic Dussault,<sup>1</sup> Stephane Salmieri,<sup>1</sup> Agnes Safrany,<sup>2</sup> Monique Lacroix<sup>1</sup>

<sup>1</sup>INRS-Institute Armand-Frappier, Institute of Nutraceuticals and Functional Foods, Research Laboratories in Sciences Applied to Food, Canadian Irradiation Center, University of Quebec, Laval, Quebec H7V 1B7, Canada

<sup>2</sup>International Atomic Energy Agency, Vienna International Centre, Vienna A-1400, Austria

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

**ABSTRACT:** Carbon nanotube (CNT) reinforced (0.05–0.5% by wt) polycaprolactone (PCL)-based composites were prepared by compression molding. Addition of 0.2% CNT caused a 131% improvement of tensile strength (TS) of PCL films. The tensile modulus (TM) and elongation at break (Eb) of PCL were also significantly improved with the addition of CNT. The water vapor permeability of PCL was 1.51 g-mm/m<sup>2</sup>-day but 0.2% CNT containing PCL films showed 1.08 g-mm/m<sup>2</sup>-day. Similarly, the oxygen transmission rate (OTR) of PCL films was found to decrease with the addition of CNT. But, carbon dioxide transmission rate (CO<sub>2</sub>TR) of PCL film was improved due to incorporation of CNT. Effect of gamma radiation on PCL films and CNT reinforced PCL-based composites were also studied. The TS of the irradiated (10 kGy) PCL films gained to 75% higher than control sample. The TS of the 0.2% CNT reinforced composite film was reached to 41 MPa at 15 kGy dose. The barrier properties of non-irradiated and irradiated (10 kGy) PCL films and composites (0.2% CNT reinforced) were also measured. Both PCL films and composites showed lower values of WVP upon irradiation and indicated better water vapor barrier. The OTR and CO<sub>2</sub>TR of the irradiated (10 kGy) PCL films and composites were decreased compared to their counterparts. Surface and interface morphologies of the composites were studied by scanning electron microscopy. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** carbon nanotubes; PCL; barrier properties; OTR; gamma radiation

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### INTRODUCTION

Nanotechnology has gained huge attention to the scientists in recent years because of manipulating materials at the level of atoms and molecules to alter the product properties drastically. In nanotechnology, materials are reduced to the nanoscale which can show significantly different properties compared with what they exhibit on a macroscale, enabling unique applications. For packaging sectors, this nanotechnology is of great demand due to its excellent potentiality. For making high performance packaging materials with improved thermo-mechanical and barrier properties, nanomaterials can be used. The important nanomaterials are carbon nanotube (CNT), nanocrystalline cellulose, and chitin/chitosan nanofibers.<sup>1–4</sup> In this investigation, CNT was used which is a microscopic carbon cylinder, thousands of times smaller than a human hair. It has generated huge activity in many areas of science and engineering due to their unprecedented physicochemical properties. The

unique properties of CNTs and the technological possibilities that CNT/polymer composites offer, including enhanced thermo-mechanical properties continues to attract global research interest. The CNT have diameters in the nanometer scale, are up to 10s of microns long, and can be single walled or multiwalled. Owing to high aspect ratio (>1000), high strength and stiffness at low density, the CNTs attract attention of the researchers as reinforcing fillers for a generation of new high performance low-weight polymer-based materials.<sup>5–7</sup> Over the last decade, many polymers have been employed as matrices for preparation of CNT/polymer composites.<sup>8–10</sup> Biodegradable plastics were also prepared and characterized using CNT and poly(lactic) acid.<sup>3</sup> The methods of distribution and dispersion of the CNTs within the polymer matrix plays a vital role on the properties of the final product. Melt-mixing,<sup>11</sup> solution-casting,<sup>12</sup> and *in-situ* polymerization<sup>13</sup> have all been employed for CNT polymer composite synthesis.

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At present, petroleum-based synthetic polymers are used as packaging materials due to their good thermo-mechanical and barrier properties and also for the economical reasons. Unfortunately, these materials are not biodegradable. Thus, efforts are in progress to develop alternative packaging materials, which are environment friendly. Typical materials under considerations are polycaprolactone (PCL), poly(lactic acid), poly(glycolic acid), and biopolymer-based materials. Biodegradable films made of these materials do not pose a threat to the environment. Therefore, many studies are now attempting to develop biodegradable films to approach physicochemical attributes analogous to those of petrochemical-based polymers.<sup>14,15</sup> PCL is a thermoplastic biodegradable polymer resulting from a chemical synthesis from crude oil. It is semi-crystalline, and has a glass transition temperature of about  $-60^{\circ}\text{C}$ . PCL belongs to the aliphatic polyester family and it has good water, oil, solvent, and chlorine resistance. PCL has a low melting-point ( $58\text{--}64^{\circ}\text{C}$ ) and low viscosity, and it is easy to process. It has been shown that PCL exhibited desirable characteristics as a diffusion-controlled delivery system, including biodegradability, biocompatibility, commercial availability, and affordability. It is produced via the ring-opening polymerization of caprolactone monomer. PCL can degrade in water via hydrolysis of its ester linkages. The main commercial application of PCL is in the manufacture of biodegradable bottles and films. This polymer is often used as an additive for resins to improve their processing characteristics and their end use properties. Being compatible with a range of other materials, PCL is mixed with starch to lower its cost and increase biodegradability. It is used mainly in thermoplastic polyurethanes, resins for surface coatings, adhesives, fully biodegradable compostable bags.<sup>16–18</sup>

Gamma radiation is one type of ionizing radiations. The application of gamma radiation is becoming more widespread every year. Over the past four decades, there has been a continuous and significant growth in the development and application of radiation techniques, primarily in the coating and adhesive industry. As this technique continues to develop, innovative products based on high efficiency and easy process control, a logical extension for this technology is found to be in the field of polymer composites. The use of gamma radiation offers several advantages, such as continuous operation, minimum time requirement, less atmospheric pollution, curing at ambient temperatures, increased design flexibility through process control and many more.<sup>19–22</sup> The objective of this study was to fabricate CNT reinforced PCL-based composites. Mechanical, barrier [water vapor permeability (WVP), oxygen and carbon dioxide transmission rate] and morphological properties of CNT reinforced PCL-based composites were evaluated. Effect of gamma radiation on the PCL films and composites was also carried out.

## MATERIALS AND METHODS

### Materials

CNT, multiwalled (purity  $>90\%$ , diameter  $110\text{--}170\text{ nm}$ , length range  $5\text{--}9\text{ }\mu\text{m}$ ) and PCL (granular form, molecular weight:  $70,000\text{--}80,000$ ) were purchased from Sigma–Aldrich Canada (Oakville, ON, Canada).

### Preparation of CNT Reinforced PCL-Based Films by Compression Molding

PCL films were prepared from its granules by compression molding machine (Carvar, Indiana, Model 3912) operated at  $110^{\circ}\text{C}$  under a consolidation pressure of 2 tons for 1 min. The mold containing PCL films was rapidly cooled using an ice bath for 2 min. The PCL film was taken out from the mold and kept in the desiccator before characterization. PCL were melt-blended with CNTs in a beaker with continuous stirring at  $110^{\circ}\text{C}$  then hot pressed in the same compression molding machine using same parameters.

### Film Thickness

Film thickness was measured using a Mitutoyo digimatic Indicator (Mitutoyo MFG, Tokyo, Japan) at five random positions around the film, by slowly reducing the micrometer gap until the first indication of contact.

### Mechanical Properties of the Films

The tensile strength (TS), tensile modulus (TM), and Eb of the films and composites were measured by universal tensile machine (UTM) (Tinius-Olsen, Model H5K) using a 1 KN load cell, with a crosshead speed of  $1\text{ mm/s}$  at a span distance of 25 mm. The dimensions of the test specimen were (ISO 14125):  $60 \times 15 \times 0.2\text{ mm}^3$ .

### Water Vapor Permeability (WVP) of Films

The WVP tests were conducted gravimetrically using an ASTM procedure.<sup>2</sup> Films were mechanically sealed onto Vapometer cells (No. 68-1, Twining-Albert Instrument Company, West Berlin, NJ) containing 30 g of anhydrous calcium chloride (0% Relative Humidity). The cells were initially weighed and placed in a Shellab 9010L controlled humidity chamber (Sheldon Manufacturing, Cornelius, OR) maintained at  $25^{\circ}\text{C}$  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  $10^{-4}\text{ g}$ . WVP was calculated according to the combined Fick and Henry laws for gas diffusion through coatings and films, according to the equation:  $\text{WVP (g mm/m}^2\text{ day kPa)} = \Delta w \cdot x / A \cdot \Delta P$ , 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  $25^{\circ}\text{C}$ ).

### Measurement of Oxygen Transmission Rate (OTR)

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

### Measurement of Carbon Dioxide Transmission Rate (CO<sub>2</sub>TR)

The CO<sub>2</sub> transmission rate (CO<sub>2</sub>TR) of films was measured using Mocon Permatron-C<sup>TM</sup> 4/41 (MOCON<sup>®</sup>, Minneapolis, MN). All analysis was carried out under atmospheric conditions, temperature of  $23^{\circ}\text{C}$  and 0% relative humidity. Readings were recorded as  $\text{cc/m}^2/\text{day}$ .

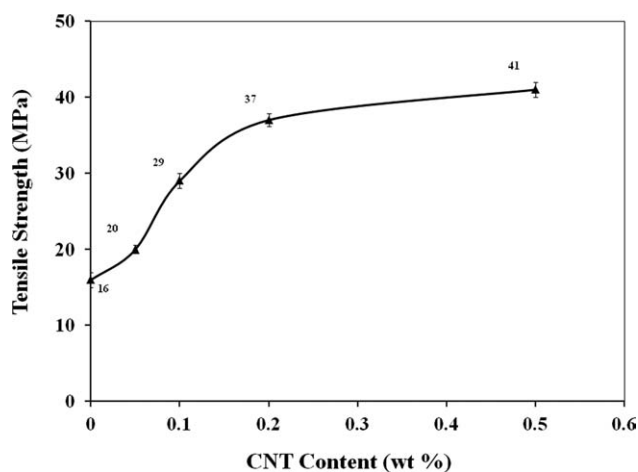


Figure 1. TS of the composite films.

### 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, 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.

### Irradiation of Films

Irradiation of films was conducted with  $\gamma$ -rays generated from  $^{60}\text{Co}$  source at room temperature, at a dose rate of 17.878 kGy/h in an Underwater Calibrator-15A Research Irradiator (Nordion, Kanata, ON, Canada).

### Statistical Analysis

All experiments were done with two replicates. For each radiation dose, three samples per treatment were evaluated. Ten radiation doses were evaluated for each experiment. An analysis of variance was performed using the PASW Statistics Base 18.0 software (SPSS, Chicago, IL), and means for each treatment were compared with Duncan's multiple range tests ( $P \leq 0.05$ ).

## RESULTS AND DISCUSSION

### Effect of CNT on Mechanical Properties of PCL Films

CNTs were mixed by blending with melted PCL then films were made by compression molding. The TS of PCL was found to be 16 MPa. Addition of minute amount CNT significantly ( $P \leq 0.05$ ) improved the TS values of PCL films. Figure 1 shows the effect of addition of CNT on PCL films. With 0.05, 0.1, 0.2, and 0.5 % (by wt) incorporation of CNT, the TS values reached to 20, 29, 37, and 41 MPa, respectively. Only 0.2% addition of CNT caused a 131% improvement of TS of PCL films. The drastic improvement of strength of PCL occurred due to the addition of CNT which has very high strength (1–2 GPa). The reinforcing effect of CNTs attributed due to the strong interfacial interaction between polymer matrix and CNTs.<sup>5–7</sup>

Similarly, TM of PCL films was also improved by the incorporation of CNT. Figure 2 shows the effect of CNT content on the

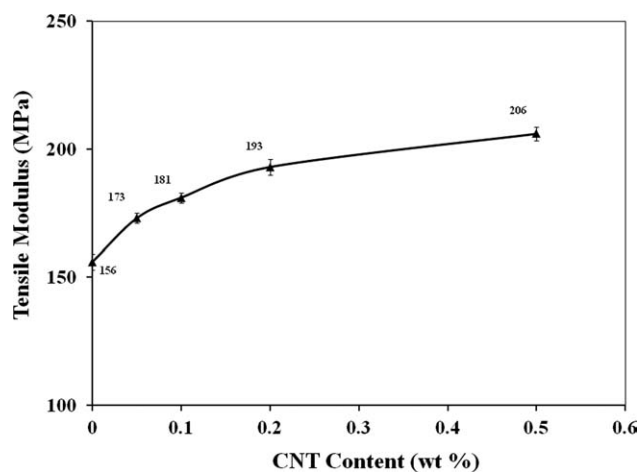


Figure 2. TM of the composite films.

TM values of PCL films. The TM of PCL films was found to be 156 MPa. The incorporation of CNT into PCL films caused a significant ( $P \leq 0.05$ ) enhanced the modulus. At 0.05, 0.1, 0.2, and 0.5% (by wt) CNT content PCL films, the TM values were found to be 173, 181, 193, and 206 MPa respectively. Thus, by incorporating only 0.2% CNT, the PCL films gained 23.71% increase of TM values. The increased TM values of the CNT reinforced PCL films may be attributed to the increased stiffness of the films by the addition of CNT. Moreover, it indicated better dispersion of CNTs in PCL matrix.<sup>7–9</sup> It is to be noted here that TM is a measure of the stiffness of an elastic material and is a quantity used to characterize materials. It is defined as the ratio of the uniaxial stress over the uniaxial strain in the range of stress. In solid mechanics, the slope of the stress–strain curve at any point is called the tangent modulus. The tangent modulus of the initial, linear portion of a stress–strain curve is called TM (or Young's modulus). It is experimentally determined from the slope of a stress–strain curve created during tensile tests conducted on a sample of the material.<sup>23</sup>

The Eb of PCL was found to be 555%. With the incorporation of CNT, the Eb values of PCL films also enhanced significantly ( $P \leq 0.05$ ). Figure 3 represented the effect of CNT on the Eb

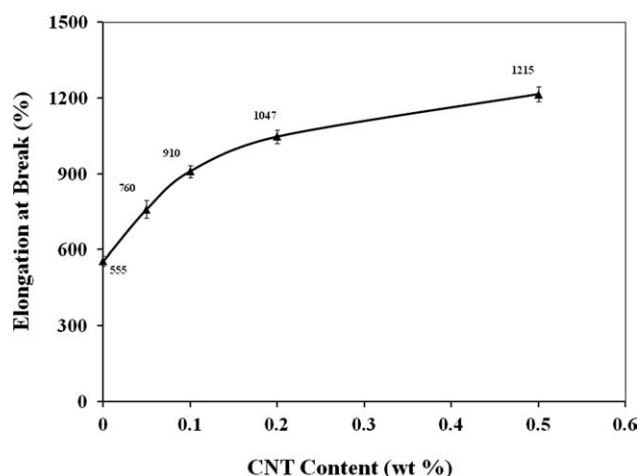


Figure 3. Elongation at break (%) of the composite films.

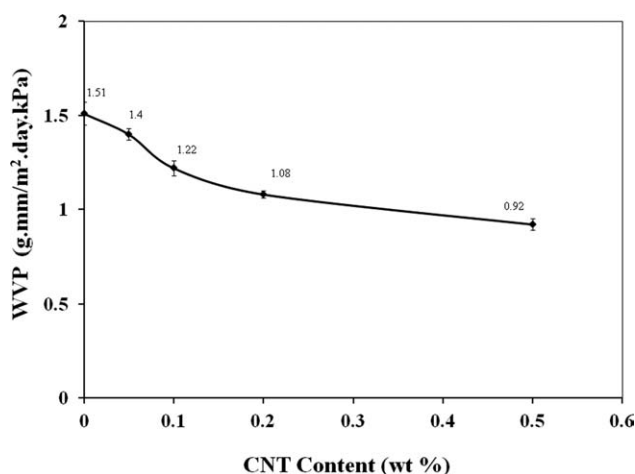


Figure 4. Effect of CNT on WVP of PCL.

(%) values of PCL films. With 0.05, 0.1, 0.2, and 0.5% (by wt) incorporation of CNT, the Eb values reached to 760, 910, 1047, and 1215%, respectively. From this investigation, this is clearly revealed that CNTs caused a significant rise of mechanical properties of PCL films. This is a rare combination that all of the tensile properties (TS, TM, and Eb) of the PCL films significantly improved with the addition of CNT. During melt blending process, CNTs were dispersed homogeneously with the matrix PCL and as a result strong interfacial interaction occurred between CNTs and PCL. Thus improved the mechanical properties.<sup>5–9</sup>

#### Water Vapor Permeability of the Composite Films

The WVP of PCL films and CNT reinforced PCL-based composites were measured. The values of WVP for PCL films was found to be 1.51 g mm/m<sup>2</sup> day kPa. Figure 4 shows the effect of CNT content on the WVP of the PCL-based composites. The values of WVP decreased continuously with increase of CNT in PCL-based films. The WVP values of 0.05, 0.1, 0.2, and 0.5% (by wt) CNT reinforced PCL films were 1.40, 1.22, 1.08, and 0.92 g mm/m<sup>2</sup> day kPa, respectively. For 0.2% CNT addition in PCL films, the WVP decreased to 39% which indicated better barrier properties. The presence of nanotubes in CNT is thought to increase the tortuosity in the PCL-based composite films leading to slower diffusion processes and hence, to a lower permeability.<sup>24</sup> The barrier properties are enhanced if the filler is less permeable and has a good dispersion into the matrix.<sup>25</sup> In this study, the interactions of CNT with PCL may have enhanced the water vapor barrier.<sup>26</sup> This can also be explained by the strong hydrophobic character of CNTs. Owing to the higher amount of hydrogen bonds, most of the biodegradable polymeric films are hydrophilic, and that is responsible for poor barriers to water vapor.<sup>27</sup> The presence of CNTs in the PCL-based composites is responsible for lower WVP values compared to control PCL films. The WVP values of the composites indicated excellent barriers to water vapor.

#### OTR of PCL and Composites

The OTR of PCL and CNT reinforced composite films was measured. Figure 5 represented the OTR of PCL, and CNT incorporated PCL films. This is clear that CNT containing com-

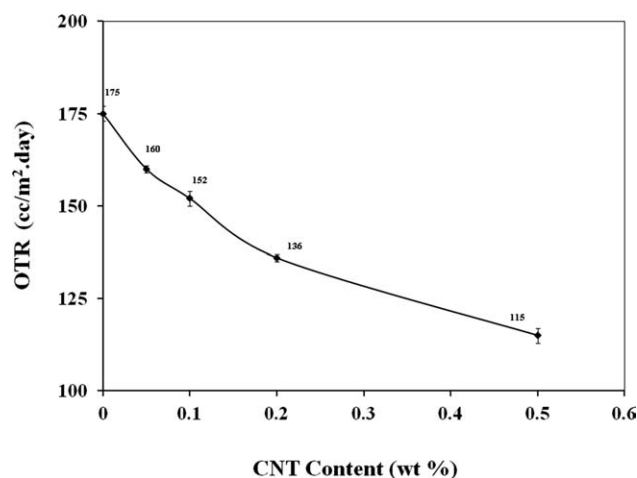


Figure 5. Effect of CNT on OTR of PCL.

posite films showed much lower OTR values than that of the PCL films. The OTR value of PCL film was found to be 175 cc/m<sup>2</sup> day. Incorporation of 0.05, 0.1, 0.2, and 0.5% (by wt) CNT in PCL films decreased OTR values to 160, 152, 136, and 115 cc/m<sup>2</sup> day, respectively. So, 0.2% CNT reinforced PCL-based composites showed a 22% reduction of 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 relative humidity.<sup>18</sup> The transfer of oxygen from the environment to food has an important effect on food quality and shelf life. Oxygen causes food deterioration such as lipid and vitamin oxidation, leading to sensory and nutrient changes. The OTR is very important since oxygen gas influence the rates of oxidation and respiration in the enclosed food, as fruits and vegetables. Generally synthetic polymers (PCL, polypropylene, polyethylene etc.) have higher OTR values.<sup>27–30</sup> Addition of CNT in PCL made a barrier to non-polar substances, such as oxygen and as a result the OTR values decreased.

#### Effect of CNT on Carbon Dioxide Transmission Rate (CO<sub>2</sub>TR)

The CO<sub>2</sub>TR value of PCL film was found to be 1170 cc/m<sup>2</sup> day. The composite films containing 0.05, 0.1, 0.2, and 0.5% CNT showed 1260, 1430, 1710, and 2240 cc/m<sup>2</sup> day kPa Figure 6 represented the CO<sub>2</sub>TR of PCL, and CNT reinforced composite films. This is clear that CNT containing composite films showed higher CO<sub>2</sub>TR values than that of the PCL films. Just addition of 0.2% CNT in PCL caused a 46% higher of CO<sub>2</sub>TR values. It is to be noted here that modified atmosphere packaging has gained considerable popularity over the last decades as a modern non-thermal 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 developed under aerobic conditions and retention of their sensorial attributes. So, the CO<sub>2</sub>TR is also very important like OTR. The CO<sub>2</sub>TR of biopolymers has low values because of its strong hydrophilic nature but the CO<sub>2</sub>TR of synthetic polymers are very high.<sup>31</sup> It is reported<sup>32</sup> that the CO<sub>2</sub>TR of high density polyethylene is 17,470 cc/m<sup>2</sup> day. This is

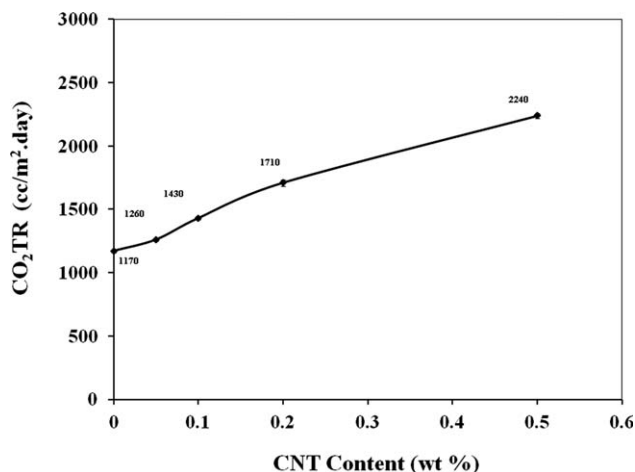


Figure 6. Effect of CNT on carbon dioxide transmission rate (CO<sub>2</sub>TR) of PCL.

because synthetic polymers are strongly hydrophobic and thus makes them less barrier to non-polar gases like carbon dioxide. When CNT was added in PCL, the CO<sub>2</sub>TR was improved because the composite was more hydrophobic in nature and thus enhanced the CO<sub>2</sub>TR.

#### Effect of Gamma Radiation on PCL and Composites

The PCL films and CNT(0.2%) reinforced PCL-based composites were exposed to gamma radiation from 2–25 kGy. Then TS, TM, and Eb of PCL and composite films were measured. The results are presented in Figures 7–9. It was found that gamma radiation had significant influence on the strength of PCL and composites (Figure 7). The TS of PCL film was found to be 16 MPa but 10 kGy irradiated films reached to 28 MPa which is 75% higher than control sample. After 10 kGy dose, the TS values decreased and reached to 22 MPa at 25 kGy dose, which is still higher than control sample. The TS of composite (0.2% CNT reinforced) film was 37 MPa but the strength of the films improved significantly (41 MPa) at 15 kGy (Figure 7). The TS value of the irradiated film improved to 11% which is much less than PCL films (75%).

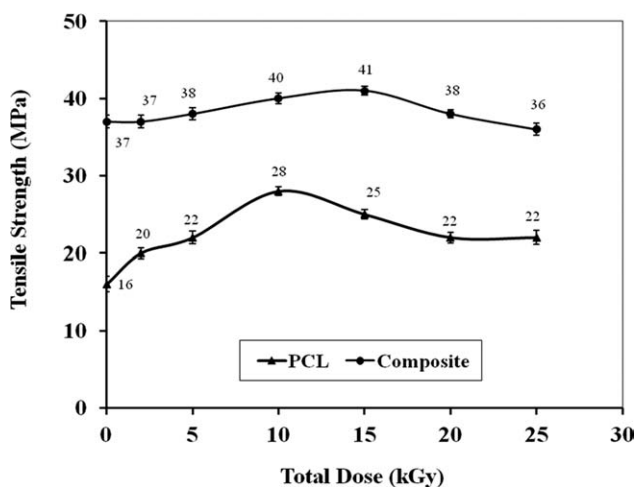


Figure 7. Effect of gamma radiation on TS of PCL and composites.

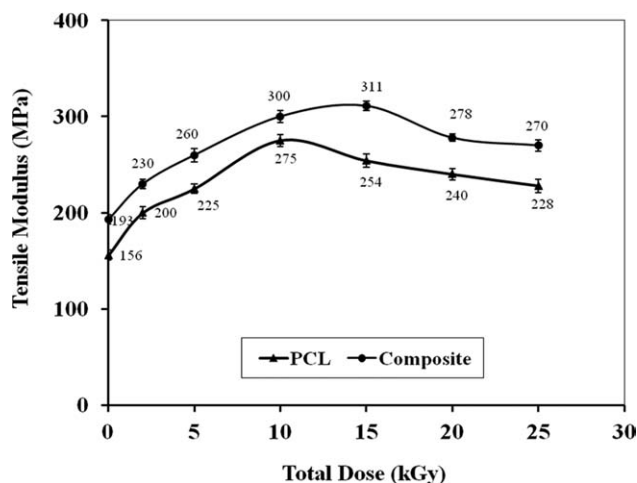


Figure 8. Effect of gamma radiation on TM of PCL and composites.

Similarly, TM values of PCL films improved significantly due to exposure of irradiation. The results are depicted in Figure 8. The highest TM value was observed at 10 kGy. The TM values of composites enhanced up to 15 kGy dose then slightly decreased and reached to 270 MPa at 25 kGy. The irradiated PCL films gained 76% higher TM values at 10 kGy than that of the control PCL films. On the other hand, composites gained 61% higher TM values at 15 kGy dose than their counterpart control composite.

An unexpected result was observed for Eb (%) values. With the rise of TS and TM values, the Eb values of the PCL films and composites were also increased with the increase of radiation dose. The effect of gamma radiation on Eb values of PCL and composites are presented in Figure 9. Both PCL and composites gained higher Eb values than their control counterpart samples. The maximum Eb values were obtained at 15 kGy dose for PCL and composites.

From this investigation, it is clear that gamma radiation has a strong role on the improvement of the mechanical properties of

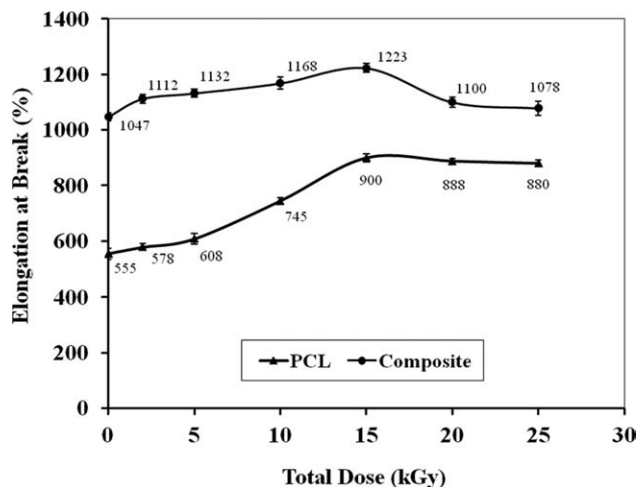
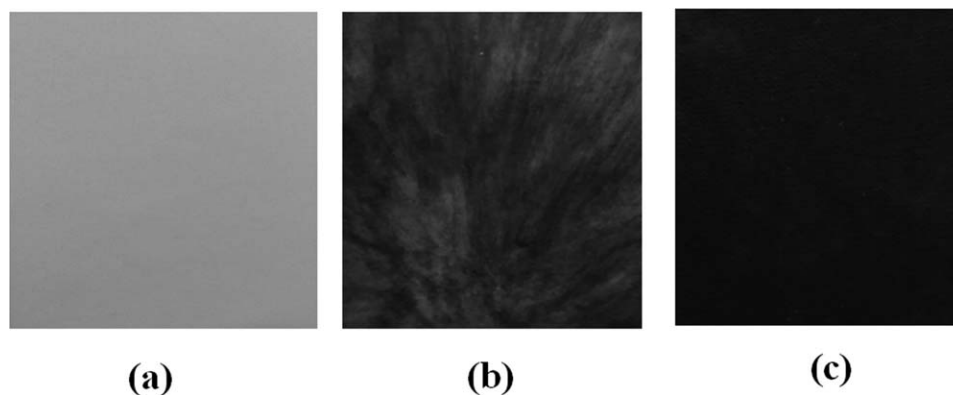


Figure 9. Effect of gamma radiation on elongation at break of PCL and composites.



**Figure 10.** Digital images of the surface of (a) PCL, (b) 0.05 wt % CNT + PCL, and (c) 0.2 wt % CNT + PCL films.

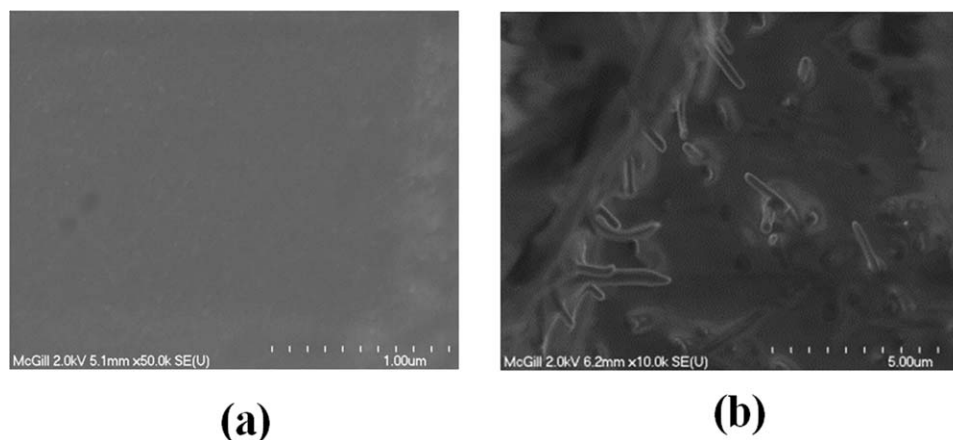
PCL films. The CNT reinforced composites showed positive trend of enhancement of mechanical properties but the intensity is much lower than PCL. The nanotubes from CNT may hinder the cross-linking of PCL and thus reduce the strong influence of irradiation for CNT reinforced composites. It is reported that<sup>33–36</sup> when polymeric materials are subjected to gamma radiation, radicals are produced on the main chain by hydrogen and hydroxyl abstraction. Gamma radiation also ruptures some carbon–carbon bonds and produces radicals. Chain scission may also take place to form other radicals. The gamma radiation produces three types of reactive species in polymer during irradiation treatment. These are ionic, radical, and peroxide. The peroxides species are produced when polymers are irradiated in the presence of oxygen. In this investigation, irradiation was carried out in presence of oxygen. So, produced peroxides may react with PCL and could produce PCL-diperoxides and PCL-hydroperoxides by a radical chain reaction process. The reaction occurs in three steps: activation, propagation, and termination. It is also reported<sup>34</sup> that the effect of gamma radiation on polymers (such as PCL) produce ionization and excitation, as a result some free radicals produce. The polymers may undergo cleavage or scission (i.e., the polymer molecules may be broken into smaller fragment). Subsequent rupture of chemical bonds yields fragments of the large polymer molecules. The free radicals thus produced may react to change structure of the polymer and also the physical properties of the materials. It also may undergo cross-linking (i.e., the molecules may be linked together into large molecules). Gamma irradiation also affects the polymeric structure and can produce active site<sup>37,38</sup>. Gamma irradiation of PCL may result in cross-linking which produces higher mechanical properties up to a certain dose. Active sites inside the polymer might be also produced by the application of gamma radiation. But at higher dose of gamma radiation on PCL could cleavage or scission molecules and thus found a decreasing tendency of mechanical properties after a certain dose.

The barrier properties of non-irradiated and irradiated (10 kGy) PCL and composites (0.2% CNT reinforced) were also measured. The WVP of PCL film was found to be 1.51 g mm/m<sup>2</sup> day kPa, but the WVP of irradiated PCL decreased to 1.32 g mm/m<sup>2</sup> day kPa which is 13% less than control PCL film. Similarly, the WVP of 0.2% CNT reinforced PCL-based com-

posites showed 9% lower values due to irradiation at 10 kGy. The values of WVP for unirradiated and irradiated composites were 1.08 and 0.98 g mm/m<sup>2</sup> day kPa. So, gamma radiation improved the water vapor barrier properties by reducing the WVP values. It is expected that during irradiation of PCL and composites, cross-linking of PCL molecules can happen and thus improved the water vapor barriers. It is reported that active sites inside the polymeric matrix might be produced by the application of gamma radiation and as a result more cross-linked structure might form and thus improved the mechanical and barrier properties.<sup>39,40</sup> Some researchers found that irradiation improved the barrier properties of the polymeric films because of hydrogen bonding involvement due to irradiation.<sup>2,22</sup> So, our results are similar in accordance with the published scientific manuscripts. A dramatic result was observed for oxygen transmission rate (OTR). The OTR of the irradiated (10 kGy) PCL increased to 224 cc/m<sup>2</sup>/day from 175 cc/m<sup>2</sup>/day. On the other hand, the OTR of the irradiated (10 kGy) PCL-based composite (0.2% CNT) increased to 152 cc/m<sup>2</sup>/day from 136 cc/m<sup>2</sup>/day. Similarly, the carbon dioxide transmission rate (CO<sub>2</sub>TR) of irradiated PCL and composites were also improved. The CO<sub>2</sub>TR of the irradiated (10 kGy) PCL increased to 1440 cc/m<sup>2</sup>/day from 1170 cc/m<sup>2</sup>/day, and the CO<sub>2</sub>TR of the irradiated (10 kGy) composite increased to 1830 cc/m<sup>2</sup>/day from 1710 cc/m<sup>2</sup>/day. PCL is partly crystalline,<sup>16,17</sup> during irradiation treatment a structural changes may occur in PCL. Both oxygen and carbon dioxide are nonpolar in nature but PCL is polar. Active sites can form in PCL during gamma radiation and also chain scission may happen. As a result, crystallinity can decrease and amorphous nature of PCL may improve<sup>41</sup> which may help to passage more oxygen and carbon dioxide.

#### Surface and Interface Morphology of the Composites

The digital images of the surface of (a) PCL, (b) 0.05% CNT + PCL, and (c) 0.2% CNT + PCL films are presented in Figure 10. The PCL films were white (a) but CNT reinforced PCL films became black (b–c). Only addition of 0.2% CNT in PCL, the films looked fully black in colour. These digital images clearly indicated the color change due to the addition of CNT in PCL matrix. The surface and interface of the CNT reinforced PCL films were investigated by SEM analysis. Figure 11 shows the SEM images of the (a) surface and (b) interface of CNT (0.2 wt



**Figure 11.** SEM images of (a) surface and (b) interface of 0.2 wt % CNT + PCL films.

%) reinforced PCL-based composites. CNTs were not appeared at the surface of composite films because only a minute amount of CNTs were added. Moreover, due to pressing at high temperature (110°C), CNTs were penetrated inside the PCL matrix which might be attributed to clear surface. Surface of this film indicated better homogenization of the CNTs with PCL. But at the interface (fracture surface) of the composites, CNTs were clearly visible. CNTs looked like fibers which imparted higher mechanical properties. The length of the CNTs used here was 5–9 μm. The SEM image showed only a fraction of the length of CNT. The remaining part of CNT was inside the polymer matrix. In the image, only 1–2 μm part of CNT is clearly visible. The interface of the composite supported above results discussed for better barrier properties also. It is reported<sup>42,43</sup> that similar types of SEM images for the interface of CNT reinforced polymer-based composites and demonstrated higher mechanical properties. So, the findings in this investigation are in well agreement with reported journals.

## CONCLUSIONS

An addition of small amount (0.05–0.5 wt %) of CNT caused a significant increase of mechanical properties of PCL films. The values of WVP and OTR of the CNT reinforced composites were reduced compared with PCL and thus indicated better moisture and oxygen barrier properties. But CO<sub>2</sub>TR of PCL films was improved by the incorporation of CNT which indicated the possibility of the prepared composite films in modified atmospheric packaging. It was noticed that gamma radiated films had better mechanical and barrier properties over the control counterpart samples. Surface and interface morphologies of the composites were studied by SEM. At the surface, no CNTs were appeared but interface morphology demonstrated the presence of CNTs and which were responsible for higher mechanical and barrier properties. This investigation opens a new door of research for packaging in modified atmospheric conditions.

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