

Modification and Characterization of Biodegradable Methylcellulose Films with Trimethylolpropane Trimethacrylate (TMPTMA) by γ Radiation: Effect of Nanocrystalline Cellulose

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ABSTRACT: Methylcellulose (MC)-based films were prepared by solution casting from its 1% aqueous suspension containing 0.25% glycerol. Trimethylolpropane trimethacrylate (TMPTMA) monomer (0.1–2% by wt) along with the glycerol was added to the MC suspension. The films were cast and irradiated from a radiation dose varied from 0.1 to 10 kGy. Then the mechanical properties such as tensile strength (TS), tensile modulus (TM), and elongation at break (Eb) and barrier properties of the films were evaluated. The highest TS (47.88 PMa) and TM (1791.50 MPa) of the films were found by using 0.1% monomer at 5 kGy dose. The lowest water vapor permeability (WVP) of the films was found to be 5.57 g·mm/m²·day·kPa (at 0.1% monomer and 5 kGy dose), which is 12.14% lower than control MC-based films. Molecular interactions due to incorporation of TMPTMA were supported by FTIR spectroscopy. A band at 1720 cm⁻¹ was observed due to the addition of TMPTMA in MC-based films, which indicated the typical (C=O) carbonyl stretching. For the further improvement of the mechanical and barrier properties of the film, 0.025–1% nanocrystalline cellulose (NCC) was added to the MC-based suspension containing 1% TMPTMA. Addition of NCC led to a significant improvement in the mechanical and barrier properties. The novelty of this investigation was to graft insoluble monomer using γ radiation with MC-based films and use of biodegradable NCC as the reinforcing agent.

KEYWORDS: methyl cellulose, trimethylolpropane trimethacrylate, biodegradable films, nanocrystalline cellulose, packaging materials

■ INTRODUCTION

Cellulose is an organic compound with the formula (C₆H₁₀O₅)_n, a polysaccharide consisting of a linear chain of several hundred to over 10000 β (1→4) linked D-glucose units. Cellulose is the most abundant organic polymer in the biosphere. It is the main constituent of plants; moreover, it is lightweight, biodegradable, and an available natural resource. The interest in using cellulosic materials as the main components in the manufacture of biodegradable packaging materials is increasing day by day. Methylcellulose (MC) is a derivative of cellulose and can be produced from cotton cellulose, wood, and annual plant pulps. It is produced by chemical treatments via alkali cellulose using a concentrated sodium hydroxide (NaOH) solution followed by treatment with methyl halide (or dimethyl sulfate). MC has been widely used for many years to produce gels and fine chemicals in pharmaceuticals, foods, construction, paints, ceramics, detergents, agriculture, polymerization, adhesives, and cosmetics. According to its physicochemical properties, MC can be also employed as an emulsifier, a medicine constituent, a colloidal stabilizer, and a viscosity and flow controller. MC is a hydrophilic white powder in pure form and dissolves in cold water, forming a clear viscous solution or gel.^{1–6} Because of its various potential uses, modification of MC was considered worthwhile to give materials with improved properties. The modification of polymers using cross-linking and grafting methods is an important commercial process for the purpose of improving the physicochemical properties of these

materials.^{7–9} Generally, polyfunctional monomers are added to achieve a high degree of cross-linking and to accelerate the cross-linking process. Trimethylolpropane trimethacrylate (TMPTMA), containing three reactive methacrylic acid residues of equal reactivity, has found wide acceptance as a cross-linking agent in poly(vinyl chloride),^{10–12} polyethylene,¹³ ethylene vinylacetate,¹⁴ and various peroxide-curable elastomers.⁷ TMPTMA also acts as a good plasticizer. It produces a high yield of radicals to facilitate grafting reactions. It is particularly effective in promoting the high-temperature creep resistance for products of polymers.⁷ TMPTMA also helps to improve cross-linking efficiency and physical properties of electron beam-irradiated polyethylene.¹³

Cellulose nanocrystals (termed nanocrystalline cellulose or NCC) are obtained by controlled acid hydrolysis of cellulose sources such as bleached wood pulp. The less-dense amorphous regions along the cellulose microfibril are more susceptible to acid attack during hydrolysis and cleave to give cellulose nanocrystals.^{15,16} These crystals are rod-like in shape with an aspect ratio that varies from 20 to 100 depending on the cellulose source. Softwood cellulose nanocrystals used in this study had an average length of 120–170 nm with a cross-section of 3–5 nm. The use of sulfuric acid to produce NCC

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suspensions imparts sulfate ester groups to the NCC surfaces during hydrolysis. The NCC particles are therefore negatively charged and aqueous NCC suspensions are electrostatically stabilized.¹⁷ Cellulose nanocrystals are recognized as being more effective than their microsized counterparts to reinforce polymers due to interactions between the nanosized elements that form a percolated network connected by hydrogen bonds, provided there is a good dispersion of the nanocrystals in the matrix.¹³ A considerable amount of research has been done on the isolation of these nanostructures from plants for use as fillers in biocomposites. It is predicted that NCC reinforcements in the polymer matrix may provide value-added materials with superior performance and extensive applications for the next generation of biodegradable materials.^{18,19}

γ radiation is a high-frequency electromagnetic radiation with a very short wavelength. As the use of γ radiation offers several advantages, the application of γ radiation is becoming more widespread every year. γ radiation has several advantages, such as continuous operation, minimum time requirement, and less atmospheric pollution. Because γ radiation is one type of strong ionizing radiation, it can produce ions for cross-linking in polymers in the absence of water or any solvent.^{20,21} When cellulosic materials are subjected to γ radiation, radicals are produced on the cellulose chain by hydrogen and hydroxyl abstraction. γ radiation also ruptures some glycosidic bonds, leading to a decrease of the cellulose chain length by random depolymerization.²⁰ γ radiation produces three types of reactive species in cellulose-based polymers. These are ionic, radical, and peroxide. The peroxide species are produced when polymers are irradiated in the presence of oxygen. The effect of γ radiation on organic polymers produces ionization and excitation, resulting in some free radicals.²¹ Over the past few decades, there has been a continuous and significant growth in the development and application of radiation techniques. The development of innovative products based on high efficiency and easy process control could be achieved with the help of this radiation technique. A logical extension of this technology was also found in the field of polymer composites.^{22,23}

The objective of the present research was to evaluate the effect of TMPTMA grafting using γ radiation on the mechanical and barrier properties of MC-based biodegradable films. Films were exposed to γ radiation from the range of 0.1–10 kGy to initiate the cross-linking of TMPTMA into MC-based films. The mechanical properties of the films were measured to evaluate their tensile strength (TS), tensile modulus (TM), and elongation at break (Eb%). Water vapor permeability (WVP) tests were carried out to investigate the moisture barrier properties of films under specified conditions. Molecular interactions of components due to the incorporation of TMPTMA in MC-based films were examined by Fourier transform infrared (FTIR) spectroscopy. Then, NCC was incorporated into MC-based films along with TMPTMA (followed by irradiation) to verify the potentiality of NCC as a reinforcing agent in MC-grafted films. The innovation of this investigation will be the grafting of TMPTMA monomer with MC-based insoluble films by γ radiation followed by reinforcing NCC to improve mechanical and barrier properties.

MATERIALS AND METHODS

Materials. MC (powder form; viscosity of 400 cP for a 1% solution at 20 °C) and monomer TMPTMA were purchased from Sigma-Aldrich Canada Ltd. (Oakville, ON, Canada). NCC was produced in an FPInnovations pilot plant NCC reactor from a commercial

bleached softwood kraft pulp according to a procedure modified from the literature (Pointe-Claire, QC, Canada). Glycerol was purchased from Laboratoire Mat (Beauport, QC, Canada).

Methods. Film Preparation. MC suspension (1%, w/w) was prepared in an ice bath using deionized water with continuous stirring. Then monomer TMPTMA (0.1–2% w/w) and 0.25% glycerol (as a plasticizer) were added to the MC suspension. The mixture was homogenized using an IKA T25 digital Ultra-Turrax disperser (IKA Works Inc., Wilmington, NC) at 45 °C and 24000 rpm for 1 min. Films were then cast by applying 15 mL of the suspension onto Petri dishes (100 mm × 15 mm; VWR International, Ville Mont-Royal, QC, Canada) and allowed to dry for 48 h, at room temperature and 35% relative humidity (RH). Aqueous NCC (0.025–1% w/w) suspension was prepared at 60 °C and sonicated for 30 min at room temperature. The NCC suspension was added to a MC-based formulation containing TMPTMA and glycerol. Then the films were cast according to the same process as described above. Dried films were peeled off and stored in polyethylene bags prior to characterization. The composition of the films on a dry weight basis is given in Tables 1 and 2.

Table 1. Concentration of TMPTMA in MC-Based (1% MC + 0.25% Glycerol) Films

TMPTMA concn in film formulation (wt %)	concn (wt %) of film components after casting (in dry film)			
	MC	glycerol	TMPTMA	total
0	80	20	0	100
0.1	74.07	18.52	7.41	100
0.25	66.66	16.67	16.67	100
1	44.45	11.10	44.45	100
2	30.76	7.70	61.54	100

Table 2. Concentration of NCC in TMPTMA-Grafted MC-Based (1% MC + 0.25% Glycerol + 0.1% TMPTMA) Films

NCC concn in film formulation (wt %)	concn (wt %) of film components after casting (in dry film)				
	MC	glycerol	TMPTMA	NCC	Total
0	74.07	18.52	7.41	0	100
0.1	68.96	17.24	6.90	6.90	100
0.25	62.50	15.63	6.25	15.63	100
0.5	54.05	13.51	5.41	27.03	100
1	42.55	10.64	4.26	42.55	100

Irradiation. Irradiation of films was conducted with γ -rays generated from a ⁶⁰Co source at room temperature, at a dose rate of 17.878 kGy/h (0.3578 kGy/min) in an Underwater Calibrator-15A Research Irradiator (Nordion Inc., Kanata, ON, Canada).

(a) **Measurement of the Mechanical Properties.** TS, TM, and Eb% of the films were evaluated by using a Universal Tensile Machine (UTM) (Tinius-Olsen Inc., USA, model HSK) 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 × 15 × 0.050 mm³.

(b) **WVP Test.** The WVP test was conducted gravimetrically using a modified procedure from ASTM test 15.09: E96.²⁴ Films were mechanically sealed onto Vapometer cells (no. 68-1, Twining-Albert Instrument Co., West Berlin, NJ) containing 30 g of anhydrous calcium chloride (0% RH). The cells were initially weighed and placed in a Shellab 9010 L controlled-humidity chamber (Sheldon Manufacturing Inc., Cornelius, OR) maintained at 25 °C and 60% RH for 24 h. The amount of water vapor transferred through the film and absorbed by the desiccant was determined from the weight gain of the cell. The assemblies were weighed initially and after 24 h for all samples and up to a maximum of 10% gain. Changes in weight of the

cell were recorded to the nearest 10^{-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

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

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 ($31.67 \times 10^{-4} \text{ m}^2$), and ΔP is the differential vapor pressure of water through the film ($\Delta P = 3.282 \text{ kPa}$ at 25°C). The value of $\Delta P = 3.282 \text{ kPa}$ was obtained directly from the *Handbook of Chemistry and Physics*,²⁵ which indicates the vapor pressure (partial pressure) of water as a function of temperature. The data (in kPa) were obtained by deducing directly from the table of the vapor pressure at 25°C for a volume fraction of 0.6 (corresponding to 60% RH).

FTIR Spectroscopy. FTIR spectra of the films were recorded using a Spectrum One spectrophotometer (Perkin-Elmer, Woodbridge, ON, Canada) equipped with an attenuated total reflectance (ATR) device for solids analysis and a high-linearity lithium tantalate (HLLT) detector. Spectra were analyzed using Spectrum 6.3.5 software. Films were stored at room temperature for 72 h in desiccators containing saturated NaBr solution to ensure a stabilized atmosphere of 59.1% RH at 20°C . Films were then placed onto a zinc selenide crystal, and the analysis was performed within the spectral region of $650\text{--}4000 \text{ cm}^{-1}$ with 64 scans recorded at a 4 cm^{-1} resolution. After attenuation of total reflectance and baseline correction, spectra were normalized with a limit ordinate of 1.5 absorbance units. The resulting FTIR spectra were compared to evaluate the effects of glycerol, TMPTMA grafting, and NC grafting, on the basis of the intensity and shift of vibrational bands.

Statistical Analysis. All experiments were conducted in duplicate, and each measurement was performed in triplicate. Analysis of variance was performed using the PASW Statistics Base 18.0 software (SPSS Inc., Chicago, IL), and means comparison between each treatment was based on Duncan's multiple-range tests ($p \leq 0.05$).

RESULTS AND DISCUSSION

Mechanical Properties. The TS values of TMPTMA-containing MC-based films were studied as a function of γ radiation dose, and the results are presented in Figure 1. The

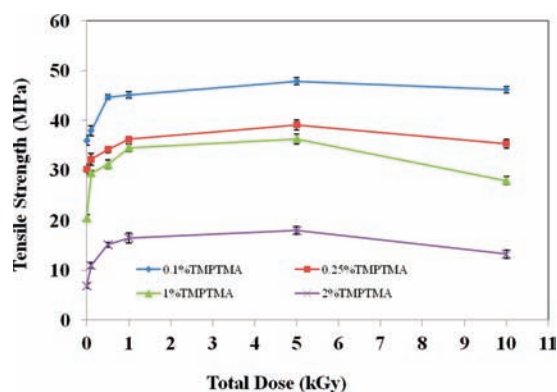


Figure 1. Tensile strength of TMPTMA containing MC-based films against total radiation dose.

TS values of MC-based films were found to be 38 MPa. With the addition of TMPTMA (denoted 0 kGy in the figure) in the MC-based films, the strength of the films decreased ($p \leq 0.05$) significantly. For MC-based films containing 0.1, 0.25, 1, and 2% TMPTMA, the TS values were found to be 36.00, 30.20, 20.45, and 6.88 MPa, respectively. Films became soft at 2% TMPTMA. TMPTMA is a low boiling point monomer,^{7–10} so addition of monomer had no positive effect on the strength of MC-based films. Moreover, our aim was to fabricate MC-based

insoluble films by grafting with insoluble monomer TMPTMA. MC-based films were readily soluble, and TMPTMA-containing films were also not stable in aqueous medium. Moreover, TMPTMA-containing films had a typical smell of monomer. γ radiation was used to react TMPTMA with MC. Actually, monomer TMPTMA did not react with MC in the absence of γ radiation, but with exposure to γ radiation (0.1–10 kGy), MC-based films were stable in aqueous medium. The values of TS of the irradiated films changed. The TMPTMA concentration in the films varied from 0.1 to 2% by wt (in film formulation). For different monomer concentrations, the TS values increased up to 5 kGy of radiation dose and then decreased (at 10 kGy). The highest TS values were observed at 0.1% monomer concentrations, which are 37.94, 44.70, 45.13, 47.88, and 46.20 MPa for 0.1, 0.5, 1, 5, and 10 kGy doses, respectively. With further increase of monomer concentration, the TS values decreased significantly ($p \leq 0.05$). The highest TS value (47.88 MPa) was observed at 0.1% monomer concentration at 5 kGy radiation dose. It is noted here that a 5 kGy dose was considered to be optimal because at this dose the films had no smell of monomer and indicated complete conversion of monomer into polymer (poly-TMPTMA), although the difference between 1 and 5 kGy was not much higher. The monomer TMPTMA might be reacted with MC molecules, and thus TS of the films increased, but at higher monomer concentration, homopolymer (TMPTMA + TMPTMA) could form and the TS values of the film decreased.²⁶ Reactive sites could be initiated in the monomers when they were irradiated, which enhances the possibility of creating chemical reaction between MC and TMPTMA. The increase of grafting led to the improvement of the TS values with increased γ radiation. However, at higher doses, polymer degradation could happen and lead to the reduction of the strength of the films.²³

TM values of the TMPTMA-added MC films are cited in Figure 2 against total radiation dose as a function of different

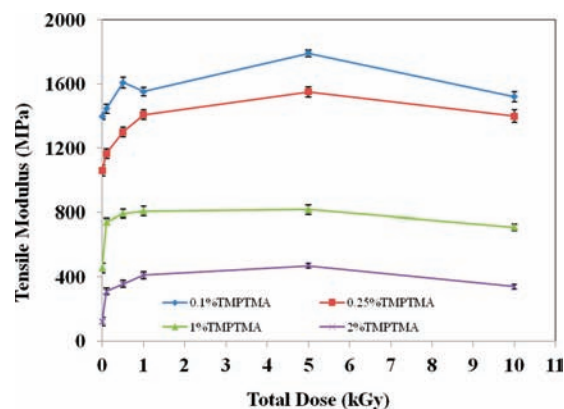


Figure 2. Tensile modulus of TMPTMA containing MC-based films against total radiation dose.

monomer concentrations. The TM of MC-based films was found to be 1640 MPa (not shown in the figure). With the addition of TMPTMA in MC-based films (not irradiated, at 0 kGy), the TM values of the films decreased significantly ($p \leq 0.05$). Addition of 0.1, 0.25, 1, and 2% TMPTMA decreased TM values of MC-based films to 1400, 1060, 457, and 122 MPa, respectively. When TMPTMA-containing MC-based films were irradiated, the TM values increased with the

increase (up to 5 kGy) of radiation dose and then decreased, but the TM values decreased at higher monomer concentrations similarly for TS values (Figure 1). For a 5 kGy dose, the TM values were found to be 1792, 1552, 818, and 470 MPa for 0.1, 0.25, 1, and 2% TMPTMA concentrations, respectively. The 0.1% monomer containing films showed better TM values. The MC films containing 0.1% TMPTMA at a 5 kGy dose showed the highest TM values. Monomer addition followed by irradiation treatment increased the TM values due to the cross-linking reaction between the monomer and the MC, but at higher monomer concentration, the TM values decreased as the monomer recombination leads to homopolymerization reaction. Again, with the increase of γ radiation dose, the TM values increased because more free radicals were initiated with the ionizing radiation, which leads to the enhanced cross-linking between TMPTMA and MC.²⁷

Flexibility and elasticity of the films are essential parameters that are considered during the application of the polymer. These two phenomena are related to the elongation at break of the film. The results of Eb values of TMPTMA-containing MC-based film as a function of γ radiation are plotted in Figure 3.

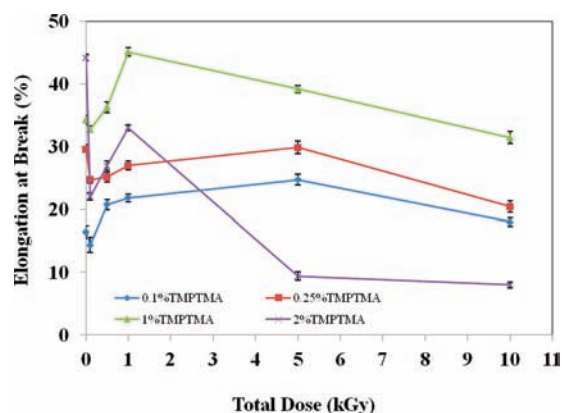


Figure 3. Elongation at break of TMPTMA containing MC-based films against total radiation dose.

The Eb value of MC-based films was found to be 14%. With the addition of TMPTMA (denoted 0 kGy in the figure) in the MC-based films, the flexibility of the films increased ($p \leq 0.05$) significantly. For MC-based films containing 0.1, 0.25, 1, and 2% TMPTMA, the Eb values were found to be 16.40, 29.50, 34.23, and 44.21%, respectively. Films became very soft at 2% TMPTMA. For 0.1 and 0.25% TMPTMA, the Eb values increased up to 5 kGy doses and then decreased. On the other hand, 1 and 2% TMPTMA containing MC-based films gained higher Eb values at 1 kGy and then decreased rapidly. The decrease of Eb values at higher doses could be related to the radiation degradation of the film.²⁸ For 5 kGy, the Eb values of the films were found to be 24.71, 29.84, 39.17, and 9.41%, respectively, for 0.1, 0.25, 1, and 2% TMPTMA concentrations. Thus, the highest Eb value (39.1%) was observed at 1% monomer concentration and 5 kGy dose. When monomer was used, it might be graft copolymerized with the MC molecules. When the films were irradiated, the hydroxyl group of MC could react with the acrylate group of TMPTMA, resulting in a cross-linked network. At low monomer concentrations (0.1–0.25%), the Eb values were increased due to inter- and intramolecular cross-linking of MC with TMPTMA, but at higher monomer concentrations (1–2%), the flexibility of the

films was lowered because of the homopolymer formation (poly-TMPTMA) or radiation degradation (breakage of polymeric bonds) of the films. As a result, at 2% TMPTMA, the Eb values decreased significantly after the 1 kGy dose. At 10 kGy, all films showed significantly lower Eb values than other doses.²⁶

Water Vapor Permeability. The WVP of MC-based films (1% MC plus 0.25% glycerol) films was found to be 6.34 g·mm/m²·day·kPa. Figure 4 shows the effect of TMPTMA on

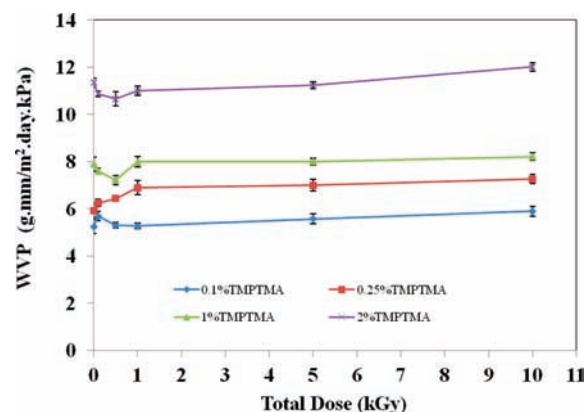


Figure 4. Water vapor permeability of TMPTMA containing MC-based films against total radiation dose.

the WVP of MC-based films as a function of γ radiation. WVP is a measure of the ease of moisture to penetrate and pass through a material. Just the addition of monomer TMPTMA (without irradiation, termed 0 in the figure) in MC-based films showed an increase of WVP. With the incorporation of 0.1, 0.25, 1, and 2% of TMPTMA, the WVP of MC-based films reached 5.24, 5.92, 7.90, and 11.35 g·mm/m²·day·kPa. A monotonous increase of WVP indicated poor barrier to water vapor through the film. When 0.1% TMPTMA containing films were irradiated from 0.1 to 10 kGy, the WVP decreased up to 1 kGy (5.27 g·mm/m²·day·kPa) and then increased, reaching 5.57 g·mm/m²·day·kPa. Similarly, for 0.25, 1, and 2% TMPTMA containing films, the minimum WVP was found for 1 kGy. After 1 kGy, the WVP values again increased with the increase of irradiation dose. The maximum WVP was observed for 2% TMPTMA content. At higher radiation doses (5 and 10 kGy), the WVP values increased significantly, which might be responsible for radiation degradation of MC molecules.²⁴

FTIR Analysis of the Films. The FTIR spectra of (a) pure MC films, (b) MC-based (with glycerol) films (control), (c) MC-based films containing 0.1% TMPTMA, and (d) MC-based films containing 1% TMPTMA are presented in Figure 5. This analysis attempted to characterize the incorporation of TMPTMA into the MC-based film matrix and distinguish the IR bands and vibration shifts related to TMPTMA interactions. The absorption peaks of the MC film spectrum (a) are mainly assignable to the stretching vibrations of O–H at 3200–3600 cm⁻¹, overlapping symmetric and asymmetric C–H at 2870–2960 cm⁻¹, and bound water vibration at 1600–1800 cm⁻¹. The pure MC (no glycerol) (a) and MC-based films (with glycerol) (b) show almost similar absorption peaks. Other bands at 1160, 1110, 1055, 1030, and 950 cm⁻¹ are attributed to typical cellulosic compounds and are assigned to C–O, C–C, and ring structures, in addition to external deformational vibrations of

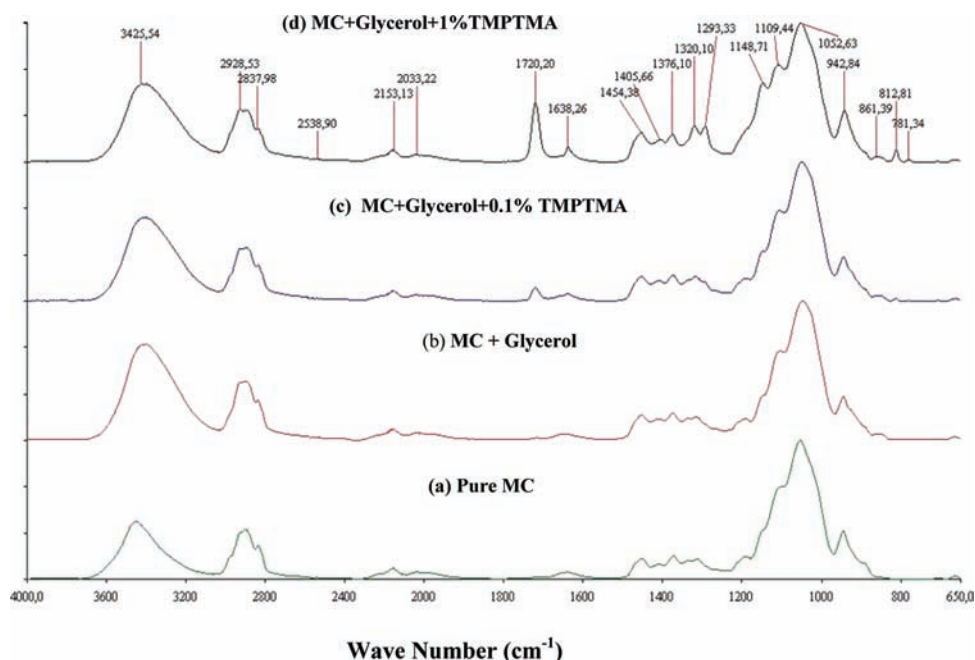


Figure 5. FTIR spectra of pure MC (a), MC + glycerol (b), MC-based + 0.1% TMPTMA (c), and MC-based + 1% TMPTMA.

CH₂, C–OH, C–CO, and C–CH groups, as already described.²⁹ Some differences can be observed in the whole IR region (for c and d) after the addition of TMPTMA into the film matrix. Indeed, a strong absorption band was observed at 1720 cm⁻¹ after TMPTMA addition for all concentrations, related to the typical (□C=O) carbonyl stretching from TMPTMA structure. The band at 1638 cm⁻¹ is due to the carbon–carbon double bond (□C=C□) stretching of the vinylidene group (c and d). The other peaks observed after TMPTMA addition at 1320, 1293, and 1148 cm⁻¹ are mainly due to the deformation vibration of the –CH₃ group, in plane deformation of –CH=CH₂ group, and the CH₂=C(CH₂)-COOR group, respectively.³⁰ In our previous studies,²⁴ a detailed FT-IR discussion on the addition of NCC in MC-based films was carried out. Similar types of peaks appeared for NCC addition in this film also.

Effect of NCC on the Mechanical Properties of TMPTMA-Grafted MC-Based Films. It was observed that a noteworthy improvement occurred in the mechanical properties when NCC (0.025–1% w/w in aqueous solution) was added to TMPTMA-containing MC-based films. The results are presented in Figure 6. It was reported above (Figure 1) that the highest TS values of the films were observed at 0.1% TMPTMA concentration and at 5 kGy radiation dose. Therefore, NCC was added to these films to determine its potentiality as a reinforcing agent. It is noted here that the TS values of MC-based, MC-based with 0.1% TMPTMA (unirradiated), and MC-based with 0.1% TMPTMA (irradiated at 5 kGy) films were found to be 38, 36, and 47.88 MPa, respectively. From the figure, it is clear that the TS values increased significantly with the increase of NCC concentration, but the TS values seemed to reach a plateau after 0.25% NCC. The TS values increased up to 5 kGy dose and then decreased. The TS values of the 0.25% NCC added films were found to be 55, 61, 68, 69, and 67 MPa for 0.1, 0.5, 1, 5, and 10 kGy doses, respectively which are 46, 37, 53, 44, and 46% higher than the TS values of the MC-based films grafted (5 kGy) with 0.1% TMPTMA films for the same radiation dose. The TS values

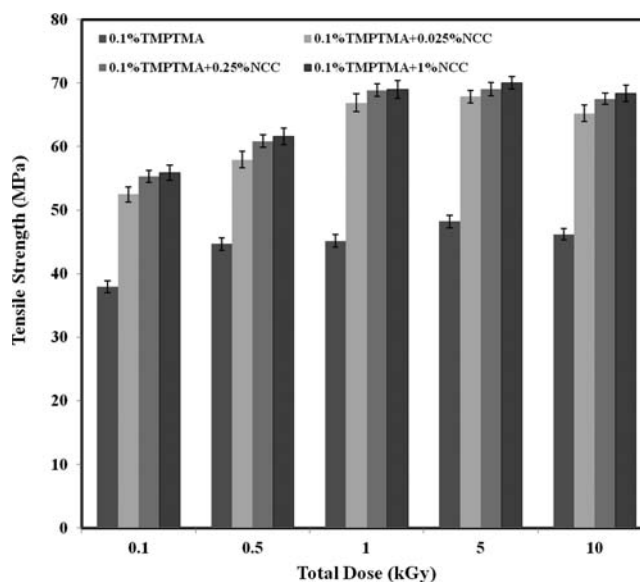


Figure 6. Effect of nanocrystalline cellulose on the tensile strength of TMPTMA-grafted MC-based films against total radiation dose.

seemed to reach a plateau after 0.25% NCC content in MC-based films. From this investigation, this clearly reflected the significant effect on the mechanical properties of NCC in MC-based films. Thus, the NCC acted as a reinforcing agent in MC-based films and is responsible for the higher TS values of the films. Similar observations were reported by Azeredo et al.³¹ They mentioned that the mechanical properties, except elongation, were improved significantly by the addition of cellulose nanofibers to mango puree edible films.

A similar trend was observed for the TM of the TMPTMA-grafted MC-based films when NCC was added to it, which is shown in Figure 7. For 0.25% NCC addition the observed TM values were 1979, 2072, 2149, 2202, and 2132 MPa for 0.1, 0.5, 1, 5, and 10 kGy doses, respectively. Thus, there were 37, 29, 38, 23, and 40% improvements in the TM values for 0.25%

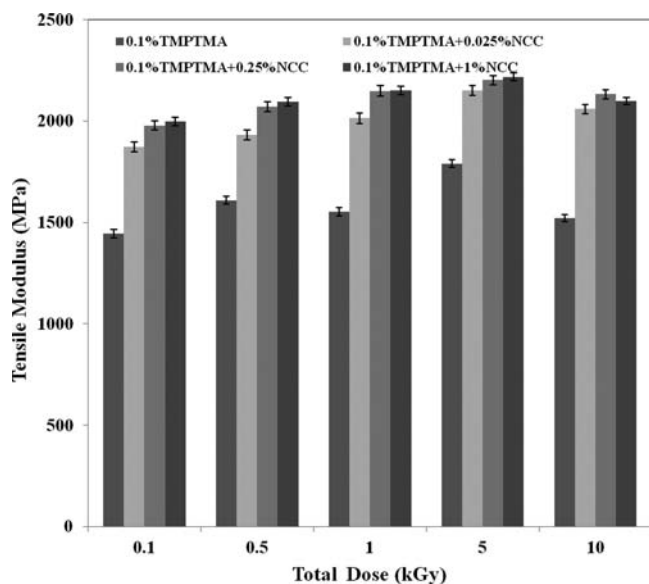


Figure 7. Effect of nanocrystalline cellulose on the tensile modulus of TMPTMA-grafted MC-based films against total radiation dose.

NCC as compared to the only TMPTMA-grafted films for 0.1, 0.5, 1, 5, and 10 kGy doses, respectively.

Figure 8 shows the change in Eb values of TMPTMA-grafted MC-based films as a function of γ radiation when NCC is

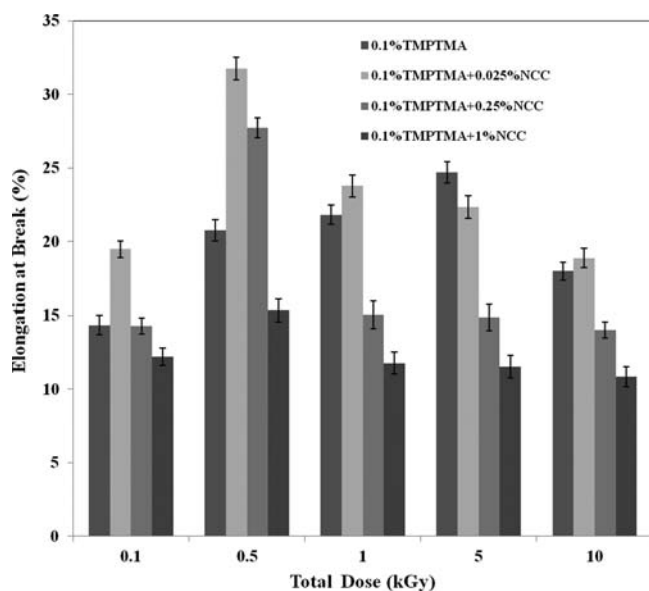


Figure 8. Effect of nanocrystalline cellulose on the elongation at break (%) of TMPTMA-grafted MC-based films against total radiation dose.

added. The Eb values increase up to 0.025% of NCC content and then decrease. Sometimes with the increase of reinforcing agent, both strength and elongation may rise. NCC is composed of nanocrystals (similar to nanorod or nanofiber). These nanocrystals can form networks with the polymer matrix and can improve elongation. A similar phenomenon is reported elsewhere.²⁴ Thus, the highest Eb values were observed for 0.025% NCC content, which is 20, 32, 24, 22, and 19% for 0.1, 0.5, 1, 5, and 10 kGy radiation doses, respectively. At higher levels of NCC, which acts as a reinforcing filler, the material tends to become somewhat more brittle. This is a common observation in nanocomposites as well as conventional composite materials. Here, NCC is acting as a reinforcing agent, so higher amounts of NCC can make the films stiffer. The decreased Eb values may be related to the increased stiffness of the films by the addition of NCC.²⁸

Effect of NCC on the Barrier Properties of the TMPTMA-Grafted MC-Based Films. The effect of NCC content on the water vapor barrier properties of the TMPTMA-grafted MC-based films is presented in Table 3. The WVP values decreased with increasing NCC content. On the other hand, at low γ radiation doses (up to 0.5 kGy), the WVP values reduced, but at higher doses (from 5 kGy) all of the samples showed higher WVP values. It is noted that the WVP value of MC-based films was found to be 6.34 g·mm/m²·day·kPa, but all of the TMPTMA-grafted films were found to have lower WVP values than the MC-based films. There was a 24% reduction in the WVP values upon 1% NCC addition at 0.5 kGy radiation dose. The presence of crystalline fibers in NCC is thought to increase the tortuosity in the MC-based films, leading to slower diffusion processes and, hence, to a lower permeability.³¹ In the present study, the interactions of NCC with MC-based film components (mainly cellulose) as well as interactions between nanofibers may have enhanced the water vapor barrier properties.²⁴

In summary, the aim of the present study was to evaluate the combined effect of the monomer TMPTMA, NCC, and γ radiation on the mechanical and barrier properties of MC-based biodegradable films. The MC is an excellent natural polymer that can be applied to various potential uses. The highest TS (47.88 MPa) and TM (1791.50 MPa) values were found at 0.1% monomer concentration at 5 kGy dose. The lowest WVP was also observed at 0.1% monomer concentration. For the further improvement of the mechanical and barrier properties of the film, 0.1–1% NCC was added to the optimal formulation. It was observed that NCC-containing films had significantly improved mechanical and barrier properties. This investigation has significant relevance to the application of packaging sectors. The prepared MC-based films are biodegradable and readily soluble in aqueous media. To protect the film from aqueous media, water-insoluble monomer was

Table 3. Effect of NCC and γ Radiation on the Water Vapor Permeability (WVP) Values of TMPTMA-Grafted MC-Based Films^a

material	WVP (g·mm/m ² ·day·kPa) at a radiation dose of				
	0.1 kGy	0.5 kGy	1 kGy	5 kGy	10 kGy
MC + 0.1% TMPTMA	5.69 ± 0.2 c	5.3 ± 0.1 c	5.27 ± 0.3 b	5.57 ± 0.2 b	5.89 ± 0.3 b
MC + 0.1% TMPTMA + 0.025% NCC	5.77 ± 0.1 c	5.48 ± 0.1 c	6.00 ± 0.2 c	6.34 ± 0.1 c	6.55 ± 0.2 c
MC + 0.1% TMPTMA + 0.1% NC	4.75 ± 0.1 b	4.42 ± 0.2 b	5.51 ± 0.1 b	5.88 ± 0.1 b	5.97 ± 0.2 b
MC + 0.1% TMPTMA + 1% NCC	4.18 ± 0.2 a	4.03 ± 0.1 a	4.69 ± 0.2 a	5.06 ± 0.2 a	5.32 ± 0.1 a

^aMeans followed by the same letter in each column are not significantly different at the 5% level.

grafted using γ radiation. Further improvement of the properties of films was carried out using NCC. This research opens a new door of preparing more hydrophobic biodegradable films for packaging applications. The novelty of this research was to fabricate insoluble films using TMPMA monomer in MC-based films followed by γ radiation and the use of the biodegradable reinforcing agent NCC.

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