

Mechanical, Barrier, and Interfacial Properties of Biodegradable Composite Films Made of Methylcellulose and Poly(caprolactone)

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ABSTRACT: Methylcellulose (MC) films were prepared by casting from its 1% aqueous solution containing 0.5% vegetable oil, 0.25% glycerol, and 0.025% Tween[®]80. Poly(-caprolactone) (PCL) films were prepared by compression molding from its granules. Biodegradable composite films were fabricated using MC film as reinforcing agent and PCL as the matrix material by compression molding. One layer of MC film was reinforced with two layers of PCL films. The MC content in the composites was varied from 10 to 50% by weight. Mechanical, barrier, and degradation properties of PCL, MC, and composite films were evaluated. The values of puncture strength (PS), puncture deformation (PD), viscoelasticity (γ) coefficient, and water vapor permeability (WVP) of the composites (50% MC content) were found to be 124.3 N/mm, 3.2 mm, 31%, and 2.6 g·mm/m²·day·kPa, respectively. Oxygen transmission rate (OTR) of PCL, MC, and composites (50% MC) were

found to be 175, 25, 22 cc/m²/d, respectively, which indicated that composite films showed significantly lower OTR than PCL films. Degradation tests of the composite films (50% MC) were performed for 6 weeks in aqueous medium (at 25°C), and it was found that composites lost its mass slowly with time. After 6 weeks, mass and PS of the composites were decreased to 13.4 and 12%, respectively. Composite interface was studied by scanning electron microscopy (SEM). The MC film had good adhesion with PCL matrix during compression molding and suggested strong interface of the composite system. SEM image after 6 weeks of degradation showed some openings in the interface and revealed slow degradation of the MC films. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1690–1697, 2012

Key words: composites; biodegradable films; methylcellulose; packaging materials; poly(caprolactone)

INTRODUCTION

Currently, petroleum-based synthetic polymers such as polyethylene, polypropylene, and polyvinyl chloride (PVC), which are not biodegradable, are widely used as packaging materials. These polymers have good thermomechanical properties and are light weight and low cost. However, these polymeric materials are creating environmental pollution. Therefore, scientists are investigating alternative packaging materials that are environment friendly, cheap, light weight, possess good thermomechanical properties, and provide a good barrier to moisture and gas. Cellulosic materials are biodegradable and

can be the alternative of synthetic polymers. Biodegradable films made of these materials will not be a threat to the environment; moreover, these will be cost effective. However, these films have poor thermomechanical properties and are strongly hydrophilic. Scientists are now focusing to overcome these difficulties.^{1–5}

Cellulose is the most abundant organic polymer. It is the main constituent of plants. Cellulose is a homopolysaccharide, which is the main constituent of wood and is composed of $\beta(1\rightarrow4)$ linked glucopyranose units. Each repeating unit contains three hydroxyl (—OH) groups. These hydroxyl groups have the ability to form hydrogen bonds. Cellulosic materials have good mechanical properties. They are also light weight, biodegradable, and widely available. A major interest is going on to use cellulosic materials as main components in the manufacture of biodegradable packaging. Plant-derived cellulose is already being used extensively in the paper and textile industries.^{6–8}

Methylcellulose (MC), a biodegradable polymer, is a modified type of cellulose, which is the most abundant biopolymer in nature. It is well known and of interest to be used as environment-friendly products, especially as coating or mulching film, because of its

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large availability, low cost, and easy processability. However, because of the biodegradable behavior of MC, it can be used only in limited applications. MC can be produced from cotton cellulose, wood, and annual plant pulps. MC has been widely used to produce gels and fine chemicals in pharmaceuticals, foods, paints, ceramics, detergents, agriculture, polymerization, adhesives, and cosmetics for many years. According to their physicochemical properties, MCs can be also used as emulsifiers, medicine constituents, colloidal stabilizers, viscosity controllers, and flow controllers. High-viscosity MCs are usually used as rheological controllers, whereas low-viscosity MCs are usually used in pharmaceutical products such as tablet-coating additives. MC shows good solubility in water at low temperature.^{9–13}

Poly(caprolactone) (PCL) is a thermoplastic biodegradable polymer resulting from a chemical synthesis from crude oil. It is semicrystalline and has a glass transition temperature of approximately -60°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 using a catalyst such as stannous octanoate. PCL can degrade in water via hydrolysis of its ester linkages.^{14–17} 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. Because PCL is compatible with a range of other materials, it can be mixed with starch to lower its cost and increase biodegradability or it can be added as a polymeric plasticizer to PVC. It is used mainly in thermoplastic polyurethanes, resins for surface coatings, adhesives, and synthetic leather and fabrics. It also serves to make stiffeners for shoes and orthopedic splints and fully biodegradable compostable bags, sutures, and fibers.^{18–20}

The objective of this study was to evaluate the mechanical, barrier, and interfacial properties of MC films reinforced PCL-based biodegradable films. The mechanical properties of the composite films were measured to evaluate their puncture strength (PS), puncture deformation (PD), and viscoelasticity (Y). Water vapor permeability (WVP) and oxygen transmission rate (OTR) measurements were performed to investigate the moisture and oxygen barrier properties of films in specific conditions. Interfacial properties were investigated by scanning electron microscopy (SEM).

MATERIALS AND METHODS

Materials

MC (powder form, viscosity: 400 cP for a 1% solution at 20°C) and PCL (granular form, molecular weight: 70,000–80,000) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Glycerol and Tween[®]80 were purchased from Laboratoire Mat (Beauport, QC, Canada). Vegetable oil (Sunflower brand) was obtained from a local grocery.

MC-based film preparation

The composition of the MC-based film formulation (w/w) was MC (1%), vegetable oil (0.5%), glycerol (0.25%), and Tween[®]80 (0.025%). The formulation was prepared in aqueous medium. The film composition was optimized.¹ The MC solution was prepared in an ice bath using deionized water with continuous stirring. Then, vegetable oil (hydrophobic agent), glycerol (plasticizer), and Tween[®]80 (emulsifier) were directly poured into the MC solution. The mixture was then homogenized using an IKA[®] T25 digital Ultra-Turrax disperser (IKA[®] Works, Wilmington, NC) at 45°C and 24,000 rpm for 1 min. Films were then cast by applying 12 mL of the film-forming solution onto petri dishes (100 mm \times 15 mm; VWR International, Ville Mont-Royal, QC, Canada) and allowed to dry for 24 h, at room temperature and at 35% relative humidity (RH). Dried films were peeled off manually using a spatula and stored in polyethylene bags before characterization.

Composite fabrication

One stainless steel plate (15 cm \times 15 cm \times 2 cm) was taken and one release film (same dimension) was placed on it. Then, granules of PCL were taken on the release film containing the steel plate. Another release film was placed on the PCL granules and then another stainless steel plate (same dimension) was fixed on it. The sandwich construction was then placed in between two platens of compression molding machine (CARVAR, IN, Model 3912). Compression molding was operated at 120°C . Polymer (PCL) melting time in the press was 3 min. First, 1 ton pressure was applied for 15 s and then up to 2 ton pressure was applied on the sandwich construction for another 15 s (total 30 s and 2 ton pressure). After that, the mold was immersed in ice bath for 30 s for cooling. PCL film was taken out from the mold and kept in a desiccator before composite film fabrication. The thickness of the PCL films (120–125 μm) and composites (130–140 μm) was maintained almost constant. Stainless steel shim was used to control the thickness of PCL and composites. However, the weight of MC-based films varied during casting by adding higher volume (10–30

mL) of MC solution in petri dishes. The percentage of MC in composites was maintained by varying the weight of MC films. The MC-based film content in the composite was varied from 10 to 50% by weight. In ambient condition, the composite did not lose weight even after 12 weeks of fabrication because the surface of the composite was fully covered by PCL, which is an excellent barrier to moisture and water.

Measurement of the mechanical properties

Film thickness

Film thickness was measured using a Mitutoyo Digimatic Indicator (Mitutoyo MFG, Tokyo, Japan) with a resolution of 0.001 mm, at five random positions around the film, by slowly reducing the micrometer gap until the first indication of contact.

PS and PD

PS and PD were performed using a Stevens-LFRA texture analyzer (model TA-1000; Texture Technologies Corp., Scarsdale, NY). Films were fixed between two perforated Plexiglas® plates (3.2 cm diameter), and the holder was held tightly with two screws. A cylindrical probe (2 mm diameter; scale: 0–900 g; sensitivity: 2 V) was moved perpendicularly to the film surface at a constant speed (1 mm/s) until the film ruptured. Strength values at the puncture point were used to calculate the hardness of the film. The PS values were divided by the thickness of the films to avoid any variation related to this parameter. PS was calculated using the equation: PS (N/mm) = $(9.81F)/x$, where F is the recorded force value (g), x is the film thickness (μm), and 9.81 m/s^2 is the gravitational acceleration. PD of the films was calculated from the PS curve by using the distance (mm) recorded between the time of first contact probe/film and the time of puncture point.

Viscoelasticity (Y) coefficients

Viscoelastic properties were evaluated using relaxation curves. The same puncture test procedure as described above was used, but the probe was stopped at 3 mm and maintained for 1 min. The relaxation coefficient Y was calculated using the equation $Y (\%) = [(F_i/F_f)/F_i] \times 100$, where F_i is the initial recorded value (g), and F_f is the second value measured after 1 min of relaxation. A low viscoelasticity coefficient ($Y \rightarrow 0\%$) indicates high film elasticity, whereas a high coefficient ($Y \rightarrow 100\%$) indicates high film plasticity.

WVP tests

WVP tests were conducted gravimetrically using an American Society for Testing and Materials (ASTM)

procedure.¹ 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% 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% 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). Film thickness was measured using a Mitutoyo Digimatic Indicator (Mitutoyo MFG) at five random positions around the film, by slowly reducing the micrometer gap until the first indication of contact.

Measurement of OTR

OTR was measured using an OX-TRANS® 1/50 (MOCON®, Minneapolis, MN) machine. During all experiments, temperature and RH were held at 23°C and 0%, respectively. The experiments were performed in duplicate, and the samples (dimension: 50 cm²) were purged with nitrogen for a minimum of 2 h before exposure to a 100% oxygen flow of 10 mL/min.

Degradation tests of the composites

Degradation tests of the composites were performed in an aqueous medium at room temperature (25°C). Degradation tests were performed for a period of 6 weeks. The degradation specimens (60 mm \times 15 mm \times 0.2 mm) were placed into glass vials containing 25 mL of deionized water (each sample placed into a separate glass vial). At each time point of measurement, samples were taken out and dried for 24 h at 50°C.

Statistical analysis

For each measurement, at least seven samples in each replicate were tested. Analysis of variance and Duncan's multiple-range tests were used to perform

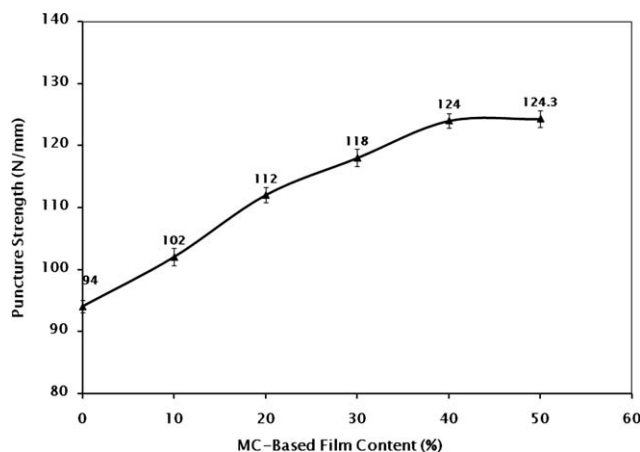


Figure 1 Puncture strength of the composite films.

statistical analysis on all results, using PASW Statistics Base 18 software (SPSS, Chicago, IL). Differences between means were considered to be significant when $P \leq 0.05$.

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 $25000\times$, 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 detector.

RESULTS AND DISCUSSION

Mechanical properties of the composite films

PS

The PS of PCL and MC-based films was found to be 94 and 147 N/mm, respectively. To increase the amount of natural polymer (MC) inside the synthetic biodegradable polymeric material (PCL), MC-based film was sandwiched (reinforced) with PCL matrix. It was expected to improve the mechanical properties and reduce barrier characteristics of the PCL-based composite films with the reinforcement of MC. Solid MC-based film (one layer), prepared by casting, was reinforced with two PCL films (prepared by hot press) using compression molding. Figure 1 shows the effect of MC content on the PS of PCL matrix composite films. The MC content in the composite was varied from 10 to 50% by weight. Incorporation of MC in PCL matrix caused a signifi-

cant increase of PS ($P \leq 0.05$). With 10% MC reinforcement, the PS of the composite films increased by 8.3% compared with PCL films (control). On the other hand, 20, 30, 40, and 50% MC contents increased the PS of composite films by 19, 25, 32, and 32%, respectively. It is clear that PS values seemed to reach a plateau after 40% MC content in PCL-based composite. Therefore, MC films acted as a reinforcing agent in PCL matrix composite films. The PS values of the PCL-based composites were increased because of higher PS values of MC (147 N/mm) compared with the PS of PCL (94 N/mm). No significant changes in PS values were observed after 40% MC addition, which indicated saturation of strength of the PCL/MC/PCL composite films. Synergistic effect in strength (i.e., higher than PCL) was not observed because of the strong hydrophilic nature of MC films compared with PCL, which is hydrophobic in nature that contributed poor interface adhesion between MC and PCL. Generally, fibers are used as reinforcing agents in conventional composites. It is reported^{21,22} that jute and phosphate glass fibers (PGFs) were used as reinforcing agents in PCL matrix and that composites gained higher tensile strength and modulus than that of PCL films. In this investigation, MC films were used as a reinforcing agent and were found potential for PCL matrix, but the intensity of improvement of strength is much less compared with fibers as reinforcing agent.

PD

The PD values of PCL and MC-based films were measured and were found to be 7.84 and 3.46 mm, respectively. Figure 2 shows the effect of MC content on the PD of PCL-based composite films. A monotonous decrease of PD values was observed with an increase of MC percentage in the composite films.

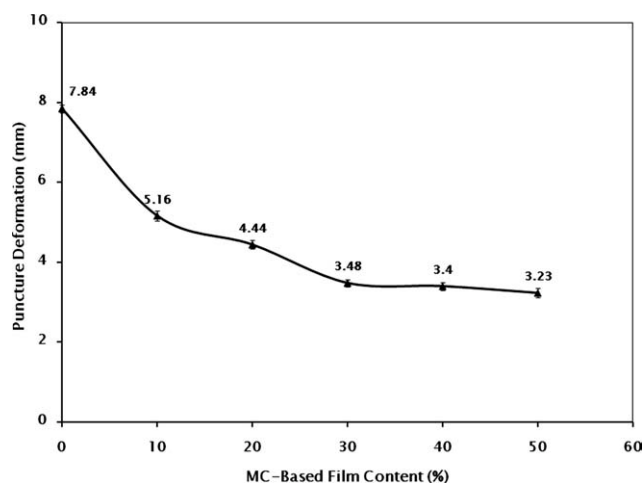


Figure 2 Puncture deformation of the composite films.

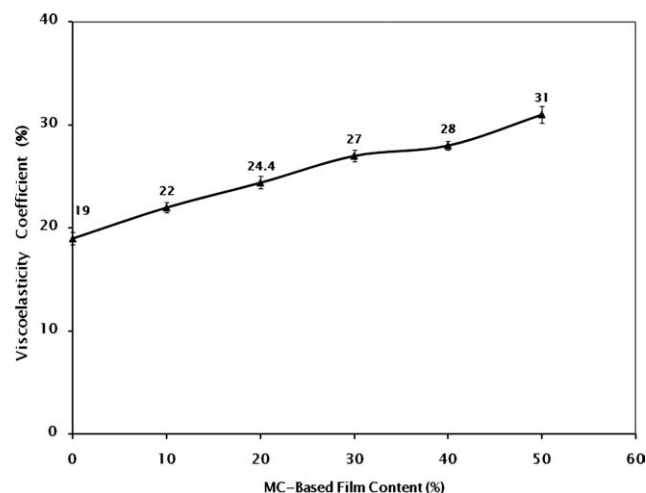


Figure 3 Viscoelasticity coefficient of the composite films.

The incorporation of MC films caused a significant decrease of PD ($P \leq 0.05$). For the addition of 10% MC film in PCL matrix, PD value of the composite decreased to 34%. For 50% MC content composite, it reached to 3.23%, which indicated a 59% decrease in PD values over PCL films. This is caused by the low PD values of MC films compared with PCL films. From this investigation, it is clear that all composite films had lower PD values than PCL films. At higher level of MC, which acts as a reinforcing material, the composite tends to become somewhat more rigid. This is a common observation in conventional composite materials.^{23–25} Here, MC is acting as a reinforcing agent in PCL-based composite films, so higher amount of MC can make the composites stiffer. The decreased PD values may be related to the increased stiffness of the composite films by the addition of MC films.

Viscoelasticity (γ) coefficient

The γ coefficient values of PCL and MC-based films were found to be 19 and 41%, respectively. Figure 3 shows the effect of MC content on the viscoelasticity (γ) coefficient of the PCL-based films. A continuous increase of γ coefficient values was observed with an increase of MC percentage in the PCL-based composite films. For 50% MC content composites, the γ coefficient value reached to 31%, which is 63% higher than PCL films but still lower than MC-based films. Because MC films have higher γ coefficient values, with increasing MC concentration, the composite films gained higher values of γ coefficient. Increase of γ coefficient values indicated a flexible nature of composite films and seemed to become more prominent with the increase of MC content. This is a promising result because PS of the composites was also improved as noted in Figure 1.

This is a rare combination in composites. Generally, with the increase in strength, the flexibility of the composites decreases.^{1,21,24} In this study, composites are made of trilayers (PCL/MC/PCL). The upper layer is PCL, which has low a γ coefficient value, but the middle layer has a high γ coefficient, as a result this uncommon nature appeared. In this investigation, the viscoelastic properties were evaluated using the relaxation curves, and the probe was stopped at 3 mm and maintained for 1 min. Because of the parameters used for this tests¹, the values of γ coefficient are closer to MC-based films.

WVP

The WVP of PCL and MC-based films was measured. The values of WVP for PCL and MC-based films were found to be 1.51 and 6.34 $\text{g} \cdot \text{mm}/\text{m}^2 \cdot \text{day} \cdot \text{kPa}$, respectively. Figure 4 shows the effect of MC content on the WVP of the PCL-based composites. The values of WVP increased continuously with increase of MC inside PCL-based films. The WVP of 10% MC content films was 1.6 $\text{g} \cdot \text{mm}/\text{m}^2 \cdot \text{day} \cdot \text{kPa}$ and reached to 2.6 $\text{g} \cdot \text{mm}/\text{m}^2 \cdot \text{day} \cdot \text{kPa}$ for 50% MC composites, which is a 82% increase compared with PCL films. This can be explained by the higher WVP of MC-based films. Owing to the large amount of hydrogen bonds, most of the biopolymeric films are strongly hydrophilic, that is responsible for poor barriers to water vapor.^{26–29} The presence of MC films in the PCL-based composites is responsible for slightly higher WVP values compared with MC-based films. However, the important finding is the drastic decrease of WVP values of the composites compared with MC-based films. The 50% MC content composites gained much higher (144%) barrier properties than MC-based films. The fabricated composites consist of three layers. The upper layer is PCL, which protects water vapor

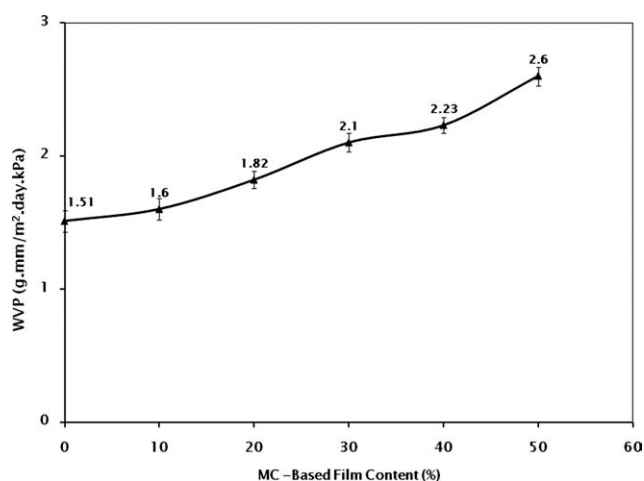


Figure 4 WVP of the composite films.

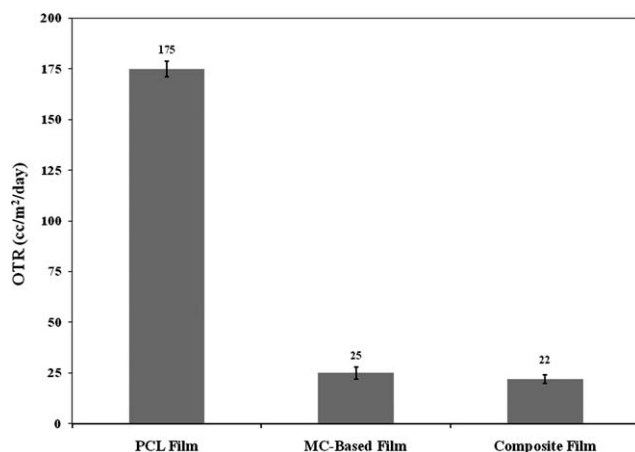


Figure 5 OTR of the composite films.

penetration and thus drastic reductions of WVP were found. It is to be noted that MC-based films are instantly soluble in water, but PCL degrades slowly.^{23,16–18} The WVP values indicated excellent barriers of the composite films in aqueous medium, which will be discussed in the later section of this article.

Measurement of OTR

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. 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. OTR is important because oxygen gas influences the rates of oxidation and respiration in the enclosed food, such as fruits and vegetables. Figure 5 represents the OTR of PCL, MC-based films, and composite (50% MC-based film content). This is clear that composite films showed much lower OTR than that of the PCL and MC-based films. Generally, synthetic polymers (PCL, polypropylene, polyethylene, etc.) have higher OTR than biopolymers (chitosan, MC, whey protein, alginate, etc.).²⁶ Because of the large amount of hydrogen bonds, biopolymer films are hydrophilic, which makes them excellent barriers to nonpolar substances, such as oxygen.^{26–29} Composite films fabricated using PCL and MC showed promising results. It is clear that composite film has even lower OTR than MC-based films, which indicated a better interface between MC and PCL. This interface and MC film (inside composite) decrease the OTR of composite films compared with PCL or the biopolymeric films (MC-based films) used as reinforcing agents.

Degradation tests of the composite films

Degradation tests of the composite samples (50% MC content) were performed in a static water bath at room temperature (25°C) for different time periods. After certain time intervals, samples were taken out from the bath and wiped using tissue paper, and then mechanical properties were measured. Figure 6 shows the loss of PS of the composite films after degradation in aqueous medium. It seems that composites lost PS continuously with time during aqueous degradation. After 2 weeks, PS of the composite decreased to 8%, whereas after 4 and 6 weeks, composites lost 11 and 12%, respectively. The reduction of strength occurred because of the presence of MC-based films (inside composite), which are strongly hydrophilic and rapidly degradable in nature. Water diffuses at the cutting edges of the composite samples, and MC films started to swell out slowly. Hydroxyl (–OH) is one of the important functional groups in MC, which causes the formation of a large amount of hydrogen bonds in the presence of water and induces their swelling. After 6 weeks of aqueous degradation, the PS of the composite reached to 109.4 MPa, which is still higher than PCL. This is a good sign that composites retained a major fraction of strength after 6 weeks by the use of MC films, which is readily soluble in water.^{9–13} The PD, γ coefficients, and WVP of the degraded samples were also investigated (not shown in figure). After 6 weeks, PD values of the composite samples reached to 5.40 mm, which is 67% higher than non degraded samples. In contrast, the γ coefficient values were down to 17% from 31%. This is caused by the degradation of MC-based films inside the composites. Values of PD and γ coefficient of

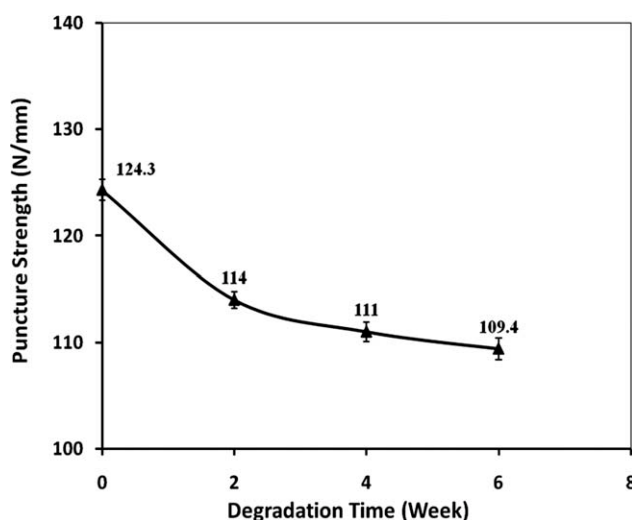


Figure 6 Mass loss of the composite films after degradation in deionized water at 25°C.

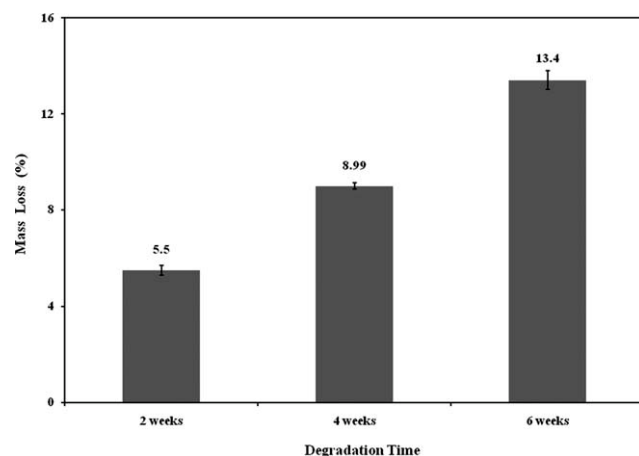


Figure 7 The loss of PS of the composite films after degradation in deionized water at 25°C.

the degraded composite samples were found to be close to PCL films. After 6 weeks of aqueous degradation, composites lost its mass. The results are given in Figure 7. After 2, 4, and 6 weeks, composite samples lost 5.5, 8.9, and 13.4%, respectively, of its original mass (i.e., weight lost). The WVP values of the degraded samples increased to 26%, which indicated less barrier properties compared with nondegraded composite films. The MC-based films, which is used as the reinforcing agent, is responsible for the weight loss of the composite samples. It is reported^{21,23} that degradable-type PGF reinforced PCL-based composites and lost its mass and tensile strength during aqueous degradation. It is mentioned that PGF is responsible for the degradation. In this investigation, MC films were used as a reinforcing agent for PCL-based composites, and results were similar to those previously reported in the literature.

Interfacial properties of the composites

Figure 8 shows SEM images of the surface of MC-based, PCL films, and composite. It seems that the surface of MC-based films is homogenous and smooth. The MC-based films were prepared by cast-

ing, and it contains vegetable oil, glycerine, and Tween®80. Surface of this film indicated better homogenization of the components with MC. On the other hand, surface of PCL films is rougher; this is caused by the release films used during hot pressing in the compression molding. The surface of the composite was also found to be similar to that of PCL films because the composite was fully covered by PCL and made using compression molding. The surface roughness appeared because of heat pressing between release films. No significant changes were observed between the surface of PCL films and composites. The fracture surface of the composite films is shown in Figure 9. SEM micrograph of the interface of MC-film reinforced PCL-based composites [Fig. 9(A)] indicated good interfacial adhesion between PCL and MC. Phases between PCL and MC are clearly distinctive. PCL phase is smooth, but MC-based films are twisted because of hot press during composite fabrication at high temperature. This is attributed to vegetable oil and glycerine. In contrast, the degraded interface [Fig. 9(B)] clearly indicated opening the interface during aqueous degradation. MC-based films are strongly hydrophilic, and thus when in contact with water, MC-based films started to degrade. Because of the degradation of MC, some channels are formed inside the interface, which is responsible for the loss of strength as reported above. Similar type of SEM images was reported elsewhere.^{21–23}

CONCLUSIONS

MC film reinforced PCL-based biodegradable composites were prepared successfully by compression molding. Mechanical (PS, PD, and viscoelasticity coefficient) and barrier (moisture and oxygen) properties of the composite films were measured. MC content in the PCL-based composite varied from 10 to 50% by weight. It was found that MC film contributed to the improvement of mechanical properties of the composites. An increase of MC content (10–50%, w/w) in films allowed increasing the PS

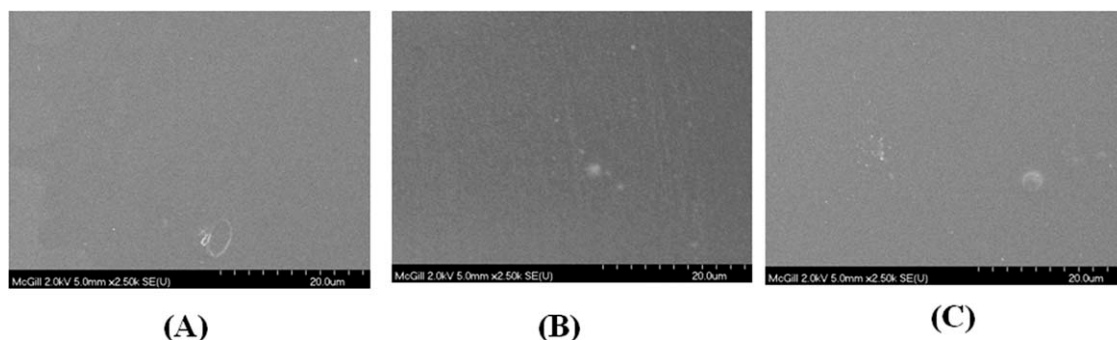


Figure 8 SEM images of the surface of (A) MC-based, (B) PCL, and (C) composite films.

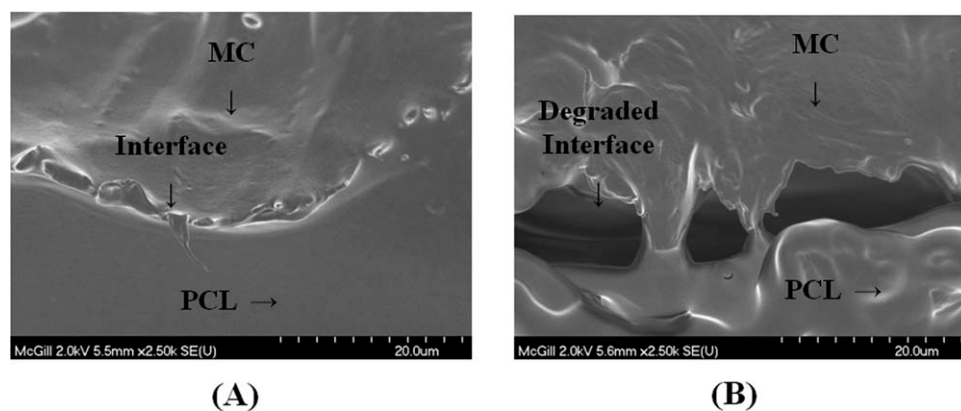


Figure 9 SEM images of the fracture surface of (A) composites, and (B) 6 weeks degraded samples.

and Y coefficient of the films significantly. WVP of the composite films was decreased compared with MC films, suggesting better barrier properties. Similarly, OTR of the composite films was decreased drastically compared with PCL, which indicates enhanced oxygen barrier properties. SEM analysis of composite interface morphology also provided justification of the improved properties obtained by MC incorporation in PCL-based composite films. In conclusion, casted MC-based films were found to be a satisfactory reinforcing agent in biodegradable PCL matrix composites by compression molding with excellent mechanical and barrier properties for packaging applications.

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