JOURNAL OF Applied Polymer SCIENCE

Special Issue: Bio-based Packaging

Guest Editors: José M. Lagarón, Amparo López-Rubio, and María José Fabra
Institute of Agrochemistry and Food Technology of the Spanish Council for Scientific Research

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Effect of hydrochloric acid on the properties of biodegradable packaging materials of carboxymethylcellulose/poly(vinyl alcohol) blends

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ABSTRACT: The main focus of this research was to prepare ecofriendly biodegradable packaging materials with carboxymethylcellulose (CMC) and poly(vinyl alcohol) (PVA). Different blend films were prepared through the variation of the ratios of CMC to PVA (00:100, 30:70, 50:50, 70:30, 100:00 w/w) with and without hydrochloric acid. The mechanical properties, including the tensile strength (TS), percentage elongation at break (E_b), water uptake, and solubility in water, of the films were investigated. A soil burial test was also performed. The prepared films were characterized by attenuated total reflectance (ATR)–Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The highest TS and E_b values of the blend films were recorded as 19.52 MPa and 34.52%, respectively. ATR–FTIR spectroscopy, DSC, and TGA results provided that in the presence of HCl, a chemical reaction occurred between CMC and PVA. In addition, the water uptake, solubility in water, and biodegradability of the films were found to be reduced significantly. With all of these results, in presence of HCl, a blend made up of CMC and PVA with a ratio 30:70 was optimized as a biodegradable packaging material. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42870.

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INTRODUCTION

Packaging materials play pivotal roles in food processing industries; we would not be able to live our normal lives without them. Mostly used packaging materials are synthetic polymers like polyethylene, polypropylene, polyolefin etc. Because of their excellent mechanical properties and chemical, weathering, and nondegradable behaviors, these plastic products are creating pollution in the environment. The shortage of petroleum materials and the adverse effects of these nondegradable plastics are great threats throughout the world. The concept of the synthetic biodegradable plastics and polymers was first introduced in 1980.[1] It is expected that materials will break down after their intended purposes and this will result natural byproducts, such as gases (CO_2, N_2), water, biomass, and inorganic salts; this is commonly known as *biodegradation*.[2,3] Biodegradation is a chemical degradation of materials triggered by the action of microbes, such as bacteria, fungi, and/or algae.[4] With regard to the demand of consumers for high-quality food and with the issue of environmental pollution kept in mind the issue, the use of renewable resources to produce edible or biodegradable/bioactive packaging materials that can maintain product quality and reduce waste disposal problems are being explored. As a substitute for nonbiodegradable, petrochemical-based counterparts, a variety of renewable biopolymers from plant and animal resources have been investigated for the development of biodegradable packaging materials.[5,6]

The application of a single biopolymer film for packaging is inadequate because of its poor mechanical properties. However, polymer–polymer interactions can be enhanced by the blending of biopolymers with biopolymers or synthetic polymers of different structures and by the introduction of largely charge interactions rather than hydrogen bonding.[7–9] However, the main drawbacks of these biodegradable films are their strong hydrophilicity and poor mechanical properties, particularly their low elongation (ca. 6%) under ambient conditions.[10] With the previous research works and aforementioned problems, in this study, we attempted to make a suitable solution with the biopolymer carboxymethylcellulose (CMC) and a synthetic polymer poly(vinyl alcohol) (PVA).

CMC is a biopolymer derived from cellulose and a copolymer of β-D-glucose and β-D-glucopyranose 2-*O*-(carboxymethyl) monosodium salts. It is water-soluble natural polymeric

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derivative having characteristic properties such as biocompatibility, renewability, and nontoxicity.[11,12] CMC is cellulose ether that shows thermal gelatinous characteristics and forms perfect films. Because of its polymeric structure and high molecular weight, it can be used as a filler for the production of biocomposite films.[13]

For fully biodegradable composites, a number of studies have been done on synthetic polymers having backbones such as poly(lactic acid), PVA, and polycaprolactone as potential materials.[14–17] PVA is a water-soluble synthetic biodegradable polymer used throughout the world[18] because of its broad applications. It exhibits characteristics of easy preparation, good film formation, strong conglutination, high thermal stability, excellent chemical resistance, good durability, and adhesive properties.[19] Biodegradable composites based on PVA have been prepared by the incorporation of natural polymers such as pea starch and cellulose.[20,21] Because of the above mentioned characteristics of PVA, researchers have focused great attention on the preparation of blend films incorporating PVA, CMC, and polymers.[22–25]

The aim of this research study was to prepare low-cost biodegradable packaging materials through the blending of CMC with PVA in the presence of hydrochloric acid. The mixing ratio of these polymers was optimized on the basis of the mechanical properties, stability, water uptake, water solubility, and biodegradable properties of the prepared films.

EXPERIMENTAL

Materials

Granular CMC of sodium salt (commercial grade) was obtained from Loba Chemical Pvt., Ltd. (Mumbai, India). PVA, with a molecular weight of 115,000 was purchased from Merck (Schuchardt OHG 85662, Hohenbrum, Germany). Hydrochloric acid (37%) was supplied from Merck (Kga A, 64271 Darmstadt, Germany). Other chemicals that were used were reagent grade.

Methods

Preparation of the Blend Films[26,27]. First, a 2% w/v CMC solution was prepared by dissolution in distilled water with continuous stirring for 1 h at 25°C.

Second, 5% w/v PVA was dissolved in distilled water through heating at about 90°C for 3 h with a hot plate and a magnetic stirrer.

Third, solutions of CMC and PVA were mixed together with different CMC/PVA ratios (0:100, 30:70, 50:50, 70:30, and 100:0 w/w). Then, 18 mL of concentrated hydrochloric acid was added to each of the mixed solutions (450 mL).

Fourth, the resulting solutions were heated at about 90°C for 2 h until the mixture became homogeneous. Finally, the films were prepared by casting on a casting plate with the humidity controlled at approximately 40–42%.

Mechanical Properties. The tensile strength (TS) and elongation at break (E_b) of the blend films were measured with a universal testing machine (Hounsfield, model H50 ks 0404, United Kingdom) by ASTM D 882-80a (1995a).[28]

Water Uptake Test. Carboxymethylcellulose/poly(vinyl alcohol) blend films with and without HCl (CPH and CP respectively) with different compositions were prepared, and the water uptake was measured. Predried films were weighed and then placed in a bath with distilled water at room temperature. After 5, 10, 15, 30, 60, 90, and 120 min and 24 h, the films were removed from distilled water, and the water uptake was measured as per the following procedure:

$$\text{Water uptake} = [(W_a - W_0) \times 100\%]/W_0$$

where W_0 is the weight of the dried sample and W_a is the weight of the sample after soaking in water.

Water Solubility Test. A modified reported method[29] was used to determine the solubility of the films in water. The films were cut into pieces (50 × 50 mm^2) and dried at 60°C for 24 h. The dried films were kept in a desiccator containing silica gel for about 30 min. Then, each of the films (with an initial weigh of W_0) was weighed, and the final dry weight was recorded as W_1. Finally, the solubility was measured with the following equation:

$$\text{Solubility} = [(W_0 - W_1) \times 100\%]/W_1$$

pH Measurement. Equal amounts from both of the untreated films and films treated with HCl were immersed in 100 mL of distilled water and stirred by a glass rod time to time for 24 h at 25°C. The pH of the resulting solutions was then measured by a digital pH meter (model Hanna, HI 2210).

Soil Burial Test. The biodegradation tests of the prepared films were done by soil burial method.[30] The dried samples were cut into 4 × 4 cm^2 specimens, weighed, and placed into soil under natural conditions. After 1, 4, 8, and 12 weeks, the samples were removed from soil, initially washed with tap water to remove the mud, and then rinsed with distilled water. The samples were then dried for 1 h 10 min at 105°C. The degree of soil degradation was calculated with the following equation:

$$\text{Degree of soil degradation} = [(W_0 - W_d) \times 100\%]/W_0$$

where W_0 and W_d are the initial and final dry weights (before and after degradation, respectively) of the blend films.

Attenuated Total Reflectance (ATR)–Fourier Transform Infrared (FTIR) Analysis. The chemical components of the model films were analyzed through ATR–FTIR spectroscopy with a PerkinElmer spectrophotometer. The spectrometer was equipped with an ATR accessory with a germanium crystal. IR light was passed through the sample with a frequency from 4000–400 cm^{-1} at a resolution of 4 cm^{-1}.

Differential Scanning Calorimetry (DSC). DSC studies of the films were performed with a PerkinElmer DSC-7 system. The vacuum-dried films were loaded, and the thermograms were run in the temperature range from 0 to 250°C under a nitrogen atmosphere at a heating rate of 10°C/min. The weights of the films used in DSC were within the range 5–10 mg.

Thermogravimetric Analysis (TGA). The thermal stabilities of the prepared films were investigated with TGA. TGA was performed with a thermogravimetric analyzer (model TGA-50, Shimadzu, Japan) within the temperature range 30–600°C with a

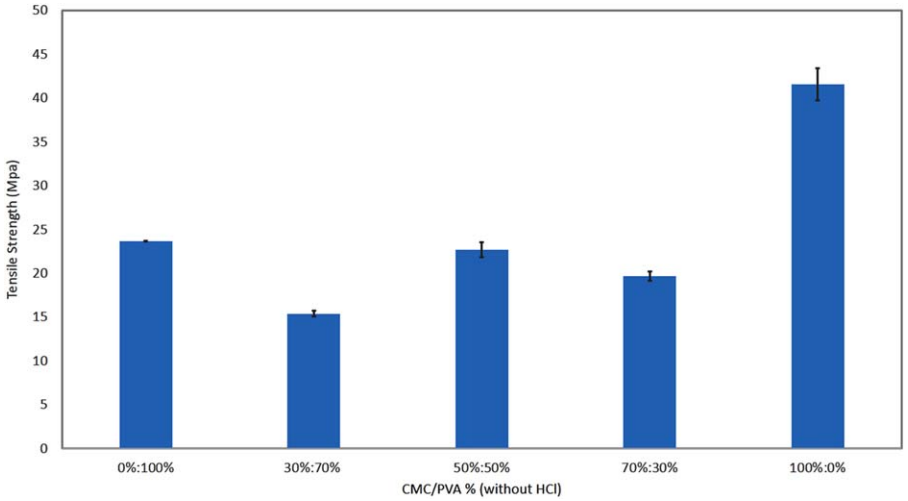


Figure 1. TS (MPa) values of different CP films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nitrogen stream as a purge gas at a heating rate of 10°C/min. The prepared films were first vacuum-dried at 100°C and loaded into the crucible for TGA.

Statistical Analysis. Statistical analysis was done with MS Excel software. The total number of repeats (n) was 5.

RESULTS AND DISCUSSION

Mechanical Properties

The TS and E_b values of different films prepared with and without hydrochloric acid are shown in Figures 1–4. The film prepared by pure PVA was normal in character, but all of the other CP films were brittle in character. HCl-treated films of pure CMC and pure PVA were also prepared, but in the case of CMC, the film was brittle and twisted. For this reason, this film was not used for further investigation. The TS values of the CMC/PVA/HCl blend films with CMC/PVA ratios of 30:70 w/w (CPH_1), 50:50 w/w (CPH_2), and 70:30 w/w (CPH_3) were found to be 19.52, 12.87, and 24.05 MPa, respectively. E_b was found to be 34.52, 19.66, and 5.22%, respectively. The reasons for the various results in different compositions could be explained as the rigid material having a high load efficiency, and as a result, it exhibited a lower elasticity. This gave a higher macroscopic strain than the polymer with no fillers.[31] Moreover, an important factor affecting the elasticity of the polymer was the substituent or chemical group attached to the monomer. If a large substitute was attached as a monomer, that created a brittle polymer. For example, polythene is more elastic than polystyrene because the monomer (ethene) of polythene is small in contrast to the monomer (styrene) of polystyrene.

The elasticity of CPH_1 was higher among other two films; this may have been due to the fact that maximum rigid CMC molecules might have taken part in the reaction to form smaller parts of the CMC molecule. This finding was compared to the study of Koc *et al.*,[32] who conducted a study with modified CMC and CMC–PVA as a miscible polymer blend; they found that the values of TS and E_b for the 50:50 w/w CMC–PVA film to be 7.44 ± 0.69 MPa and $2.42 \pm 0.52\%$, respectively. Taghizadeh *et al.*[33] investigated the mechanical properties of clay-incorporated CMC/starch/PVA composites. The values of TS and E_b of a 20% CMC/30% starch/50% PVA film were found to

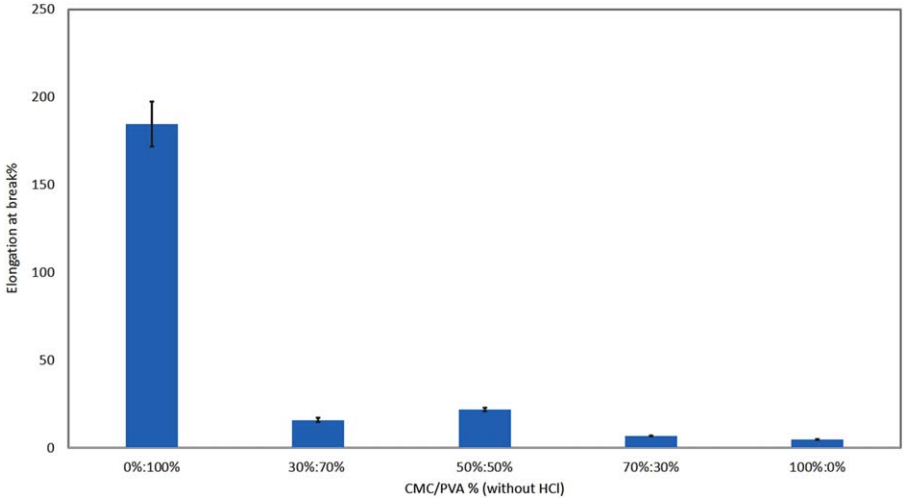


Figure 2. E_b (%) values of different CP films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

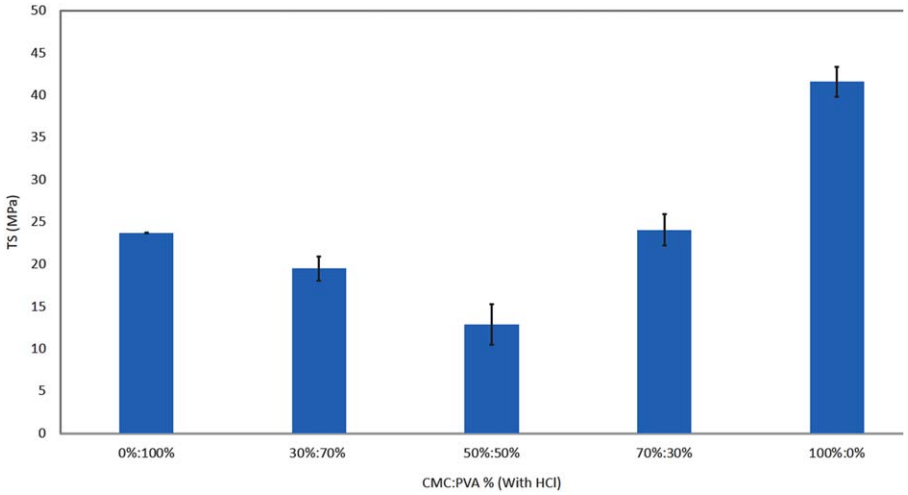


Figure 3. TS (MPa) values of pure CMC, pure PVA and different CPH films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be 18.2830 ± 0.68 MPa and 34.50 ± 0.93%, respectively. In our study, we found significantly higher values of TS and E_b for a film having a similar composition; that is, TS of CPH_1 was found to be 19.52 ± 1.43 MPa, and its E_b was 34.52 ± 0.97%. HCl was the only addition to the blend formulation compared to the blend in the previous experiment. So, the experimental results indicate that HCl induced crosslinking; this led lead to a significant increase in the mechanical properties of the films.

The CPH_2 film exhibited a lower TS but a higher E_b than that of CPH_3 (Figures 3 and 4). This may have been due to the participation of the lower amount of CMC and the higher amount of elastic PVA. Among the films, CPH_3 exhibited the highest TS and the lowest E_b; this indicated the presence of a higher number of unreacted CMC molecules, which acted as a rigid filler material.

In addition, from the experimental findings, we concluded that in the presence of HCl, macromolecules of sodium carboxymethylcellulose (Na-CMC) might have been hydrolyzed into the smaller CMC monomer or oligomer, which reacted with the PVA chain, and thus, elastic properties developed. The elasticity of the CPH_1 blend was higher than those of the other blend films; this is a favorable criterion for a good packaging materials. The TS value (19.52 MPa) was also good for a packaging material. So only this composition [30:70 w/w (CMC/PVA)/HCl] was optimized and taken into consideration for further studies.

Water Uptake and Water Solubility Tests

The water uptake and water solubility results of the different blend films are shown in Figures 5 and 6, respectively. The water absorption capacities of the pure CMC, pure PVA, and CP and CPH films were found to have significant differences. The CP films with all compositions exhibited higher water absorption capacities, and within a very short period of time, the maximum portion of the films was dissolved in distilled water. Also, the solubility of the CMC/PVA blend films (CPs) with all compositions increased with increasing CMC content; these findings were similar to those reported in other studies.[34] This indicated that without HCl, no chemical reaction occurred

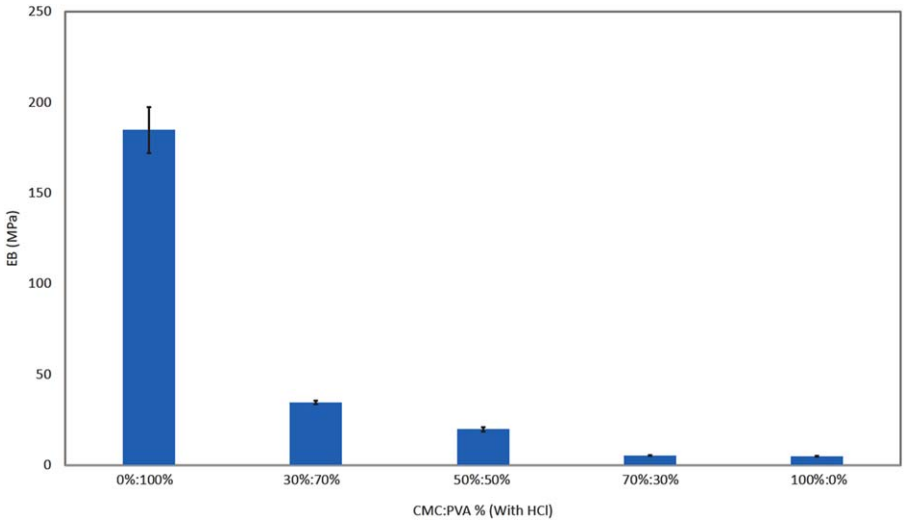


Figure 4. E_b (%) values of pure CMC, pure PVA and different CPH films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

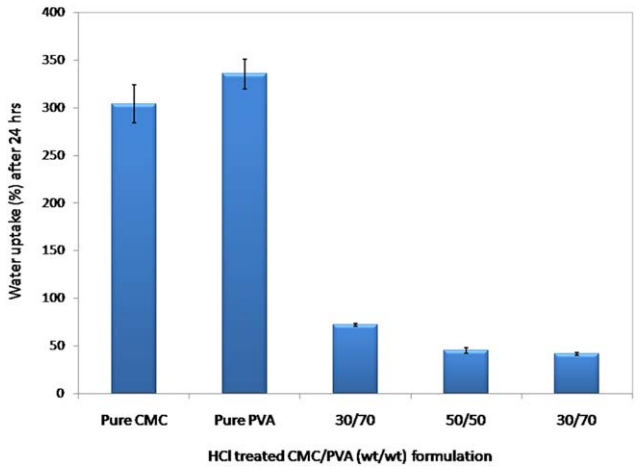


Figure 5. Water uptake values of different blend films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

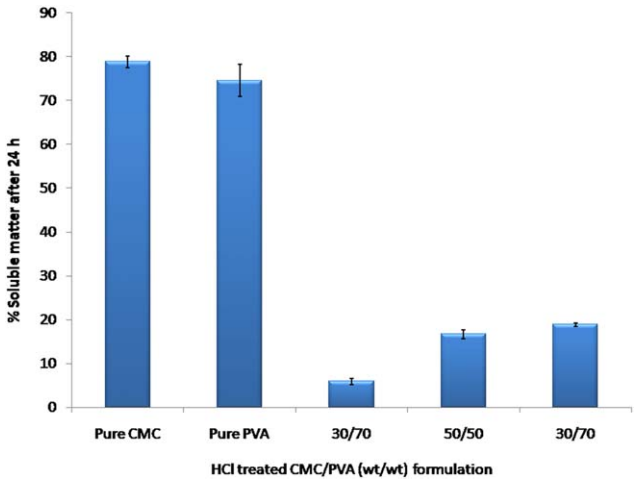


Figure 6. Soluble matter (%) of different blend films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between CMC and PVA. The pure PVA blend films were partially dissolved within 24 h. The water uptake and water solubility of the pure (100%) CMC blend film were found to be 303.74 and 78.83%, respectively. On the other hand, the water uptake and water solubility of the pure (100%) PVA blend film were found to be 335.24 and 74.58%, respectively. The reason was that with an increased CMC content, structural deformation occurred because of the true mixing of two different types of molecules; this rendered the network more hydrophilic, as a result, intermolecular attraction between CMC and PVA decreased. Moreover, in comparison to the CMC/PVA (CP) blend films, the pure CMC and pure PVA blend films exhibited lower water uptake and water solubility values; this indicated strong structural formation, higher intermolecular attraction, and strong intramolecular or intermolecular hydrogen bonding in the molecule itself. We observed that the water uptake increased with increasing PVA content. The reason was that water molecules were absorbed by the unreacted hydrophilic —OH groups of PVA through hydrogen bonding.[35]

The CPH films exhibited a minimum water uptake and lower water solubility. These results indicate that in the presence of HCl, hydrophilic —COOH groups of CMC and —OH groups of both CMC and PVA were replaced by less hydrophilic groups through chemical reactions. The percentages of soluble matter of the pure CMC, pure PVA, and different HCl-treated films (CPH_1, CPH_2, and CPH_3) were found to be 78.83, 74.58, 5.96, 16.74, and 18.87, respectively, after immersion in distilled water for 24 h. The solubility of different films was also tested for up to 72 h, but the differences were found to be very negligible between the results for 24 and 72 h. The total solids remaining insoluble (insoluble matter) after 24–72 h were found to be about 21.17, 25.42, 94.04, 83.26, and 81.13%, respectively, for aforementioned films. A similar study was conducted on a PVA/starch/CMC/sodium montmorillonite composite,[36] where researchers found solid remains of 74.53 wt % for PVA/starch/CMC, 77.87 wt % for PVA/starch/CMC/1% sodium montmorillonite, and 80.13 wt % for PVA/starch/CMC/5% sodium montmorillonite.

In our study, the results prove that the total soluble matter percentage increased when the amount of CMC increased. Among the films, CPH_1 exhibited the lowest total soluble matter percentage; the reason was that the reacted hydrophilic groups of both CMC and PVA were higher than that of other combinations. This also suggested that with increasing CMC content, unreacted hydrophilic —COOH and —OH groups increased. As a result, water molecules were absorbed through hydrogen bonding or weak electrostatic interactions. Accordingly, the film could be easily dissipated with water molecules.[35] Although the CPH_1 blend film exhibited a slightly higher water uptake, it had the lowest water solubility; this is also a suitable characteristic for good packaging materials. So, because of the mechanical properties, water uptake, and water solubility, only the CPH_1 blend film was optimized and taken in consideration for further investigations, such as ATR–FTIR spectroscopy, DSC, and TGA.

Soil Burial Tests

The biodegradation test results of different films are presented in Figure 7, and it was observed that the rate of degradation increased with increasing time. The findings were consistent with the results reported by Bastioli *et al.*[3] They stated that the biodegradation of an amylase PVA composite (PVA blend) was very slow and that in a degradation test with activated sludge, a 75% weight loss required 300 days. From this study, according to the rate of degradation of the prepared films, we concluded that the blended films would be degraded by 2–3 years. The biodegradabilities of the pure CMC and pure PVA films were also tested, but the data were not presentable as these films biodegraded very quickly.

ATR–FTIR Analysis

The combined spectra for the pure CMC, pure PVA, CP, and CPH_1 films are shown in Figure 8.The FTIR spectra of pure Na-CMC showed a characteristic strong and broad band at 3311.06 cm^{-1} because of the presence of the nonsubstituted O—H group of the anhydroglucose ring. Because this frequency was slightly lower than that of the primary hydroxyl groups around 3630 cm^{-1}, it indicated that the O—H groups were hydrogen-bonded.

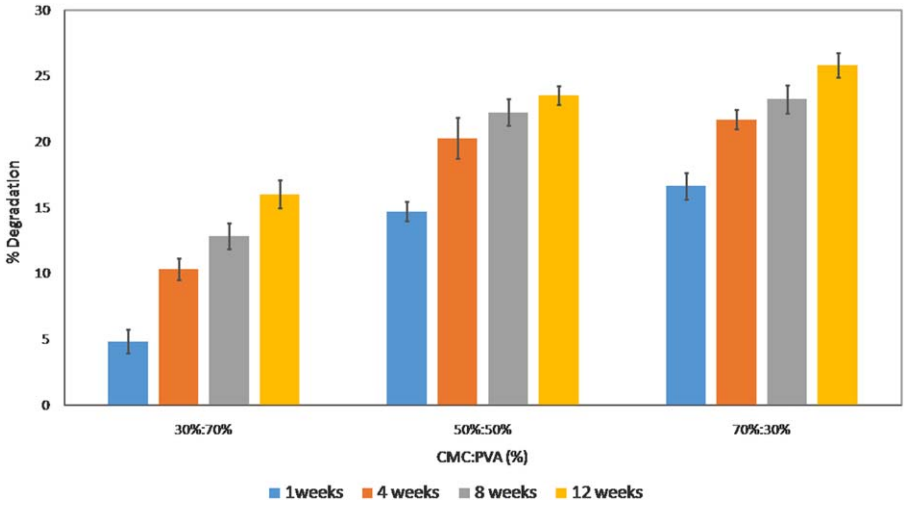


Figure 7. Biodegradability (%) versus time (weeks) for various CPH films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A weak absorption band was found at 2920.80 cm^{-1}; this was due to the C—H stretching vibrations. Characteristics absorption bands observed at about 1586.45 cm^{-1} (between 1500 and 1600 cm^{-1}) indicated the presence of —COO^- groups.[37] Two sharp bands were observed at 1413.12 and 1322.96 cm^{-1}; these were assigned to —CH_2 scissoring and —OH stretching vibrations, respectively, due to the presence of a C—H combination. Another two bands were observed at 1268.5 and 1203.96 cm^{-1}; these may have been due to the presence of a C—H second overtone or a combination or stretching vibrations of the C—O—C group. A band was observed at 911.22 cm^{-1} due to rocking vibrations. A narrow and sharp band was also observed at 1100 cm^{-1}; this indicated the presence of ether groups of —CH— O—CH_2—. Another short peak was observed at 911.22 cm^{-1}; this might have been due to the presence of —OH bending.

In the FTIR spectrum of the pure PVA, a characteristic broad band was observed at 3261.42 cm^{-1} (Figure 8) due to the presence of intermolecular and intramolecular hydrogen-bonded —OH groups. The sharp band observed at 2910.71 cm^{-1} indicated the presence of aliphatic C—H stretching vibrations. Another medium band observed at 1416.91 cm^{-1} indicated —C—C—C— bending with C—H combinations in PVA. A peak was also found at 1326.59 cm^{-1}; this was attributed to the combination frequencies of —CH and —OH. The strong absorption peak found at about 1110 cm^{-1} (between 1060 and 1150 cm^{-1}) was assigned to the C—O—C stretching mode of PVA. Two other small peaks were observed at 916.23 and 830.80 cm^{-1}; these represented O—H and C—H bending, respectively.[37]

The FTIR spectra of the film without HCl treatment (Figure 8) exhibited two broad bands around 3264.1 and 2919.28 cm^{-1} represented the presence of a hydrogen-bonded —OH group and C—H stretching vibrations, respectively. These bands were very similar to those of the pure CMC and PVA and indicated the presence of nonsubstituted O—H groups and C—H stretching vibrations. A peak was also observed at 1598.08 cm^{-1} for

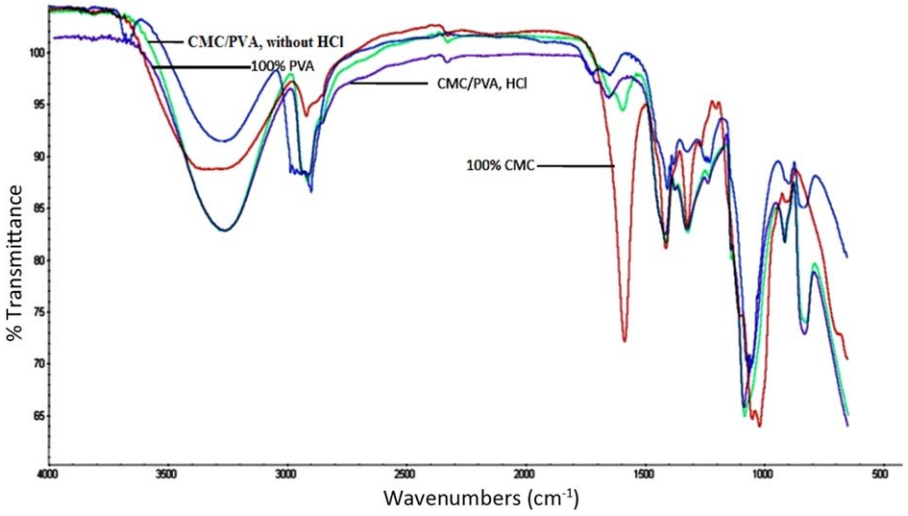
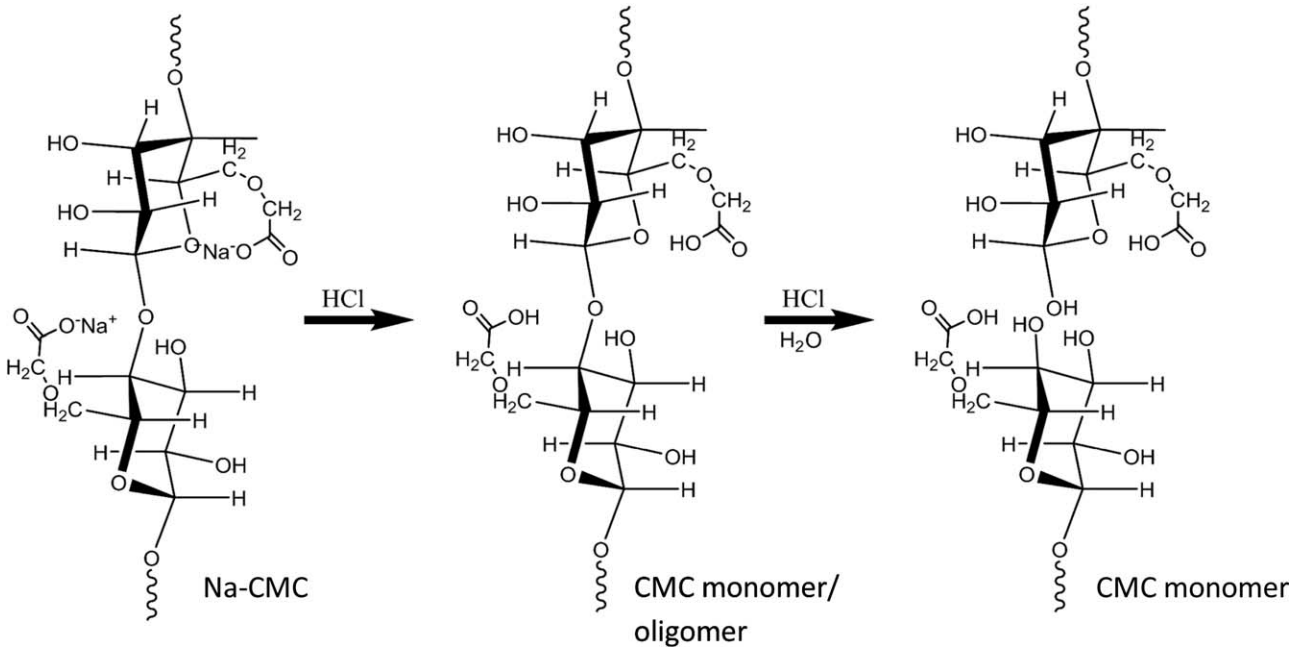


Figure 8. FTIR spectra of the pure CMC, PVA, CP with 30:70 CMC/PVA, and CPH_1 films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1. Degradation of CMC into lower molecular weight CMC such as CMC monomer or oligomer.

the —COO^- group; it was shifted slightly from that of pure CMC (1586.45 cm^{-1}). This shift may have been due to the formation of hydrogen bonds between —COO^- of the CMC and —OH groups of PVA. Four similar bands to those of pure CMC and PVA were found at 1416.88 cm^{-1} (for pure PVA, 1416.91 cm^{-1}), 1377.61 cm^{-1} (for pure PVA, 1326.59 cm^{-1}), 1323.77 cm^{-1} (for pure CMC, 1322.96 cm^{-1}), and around 1100 cm^{-1} (for both CMC and PVA, about 1100 cm^{-1}); these were due to the presence of asymmetric —COO^- groups, —OH stretching vibrations, and C—O—C groups.

A narrow peak observed at 1236.15 cm^{-1} was due to the presence of C—H second overtones; this peak was slightly shifted to a lower frequency compared with that of the pure CMC (1268.5 cm^{-1}). This may have been due to the formation of H bonds between O—H of CMC with the neighboring O—H of PVA. From the previous ATR–FTIR results, we concluded that in the absence of HCl, there was no chemical reaction in the CMC/PVA blend; it was a true mixture.

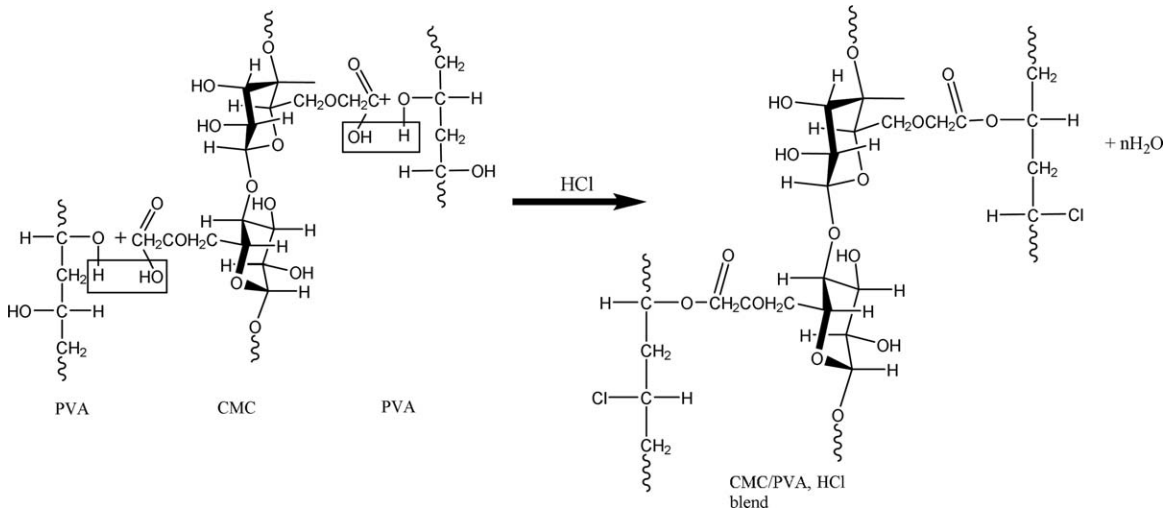
The FTIR spectra of the CPH_1 blend film revealed different features (Figure 8), in which some absorption bands changed significantly. A very small and weak peak was observed at 3675.07 cm^{-1}, whereas in the case of pure CMC and pure PVA, the bands were very long and broad. This indicated that somehow, maximum —OH groups were replaced and fewer primary O—H hydroxyl groups were present. A short and broad band was observed at 3274.33 cm^{-1} and was due to the presence of H-bonded O—H stretching, whereas in the pure CMC and pure PVA, these peaks were observed at 3311.06 and 3261.42 cm^{-1}, respectively. Four very narrow and diffuse bands were observed at 2970.34, 2987.79, 2943.21, and 2900.86 cm^{-1} and were due to C—H stretching vibrations. A small peak observed at 1732.44 cm^{-1} indicated the presence of aliphatic carbonyl groups (C═O) and the stretching vibrations of ester; another small peak also observed at the frequency 1652.22 cm^{-1} indicated carboxylic C═O stretching. Very narrow and small peaks observed at 1249.69 and 1230.79 cm^{-1} indicated the presence of C—O stretching in esters, ethers, alcohols, and alkyl halides (chloride). A strong band observed at 1027.7 cm^{-1} was due to the presence of C—O stretching vibrations. A peak at 898.66 cm^{-1} corresponded to the peak at 834.74 cm^{-1} and indicated the presence of C—Cl stretching. These observations supported the fact that some —OH groups were also replaced by Cl^- ions. So, the previous information suggested that in the presence of hydrochloric acid, a chemical reaction occurred in the CPH_1 blend film.

Probable Reaction Scheme

In the presence of hydrochloric acid, the CMC/PVA films exhibited higher TS and E_b values, lower water uptakes, and lower solubility. The absorption bands (as determined by FTIR spectroscopy) of the CMC/PVA/HCl blend also differed from those of the CP film. In addition, in the presence of HCl, film formation of pure CMC was not possible; this revealed that Na-CMC must have been hydrolyzed into smaller molecules. All of these suggested that chemical reactions must have occurred between CMC and PVA. With this information, we propose the following reaction mechanisms.

Step 1. First, in the presence of hydrochloric acid, Na-CMC might have been hydrolyzed into a lower molecular weight CMC, such as a CMC monomer or oligomer (Scheme 1).

Step 2. Next, the CMC monomer or oligomers took part in the esterification through the —OH groups of the carboxymethyl groups (—CH_2OCH_2COOH) themselves and the —OH groups of PVA. At the same time, some of the excess —OH groups of CMC or PVA or both might have been replaced by Cl^- ions. This depended on how many hydroxyl groups took part in the



Scheme 2. Esterification of CMC monomer/oligomer with hydroxyl group.

reaction and the chain length of the CMC and PVA backbone structure. FTIR analysis provided sufficient evidences in favor of this (Scheme 2).

pH Measurement

Amounts of 0.5 g of both the CP blend film and the CPH_1 blend film were immersed in 100 mL of distilled water for 24 h at 25°C. The CP blend film dissolved in distilled water, but physically, CPH was insoluble. The pHs of the resulting suspension/solution of the CP and CPH_1 blend films were 7.20 and 4.70, respectively. So, the results suggested that the pH effect for CP and CPH_1 due to the addition of HCl was not significant. The evidence shows that soft drinks have a pH of around 2.5 and lemon has a pH of about 2.0 (https://springsoralhealth.wordpress.com/2012/02/01/ph-of-soft-drinks/). Moreover, the human stomach contains HCl along with other stuff and has a pH values from 1.5 to 3.5. (https://thechronicleflask.wordpress.com/2013/08/28/amazing-alkaline-lemons/). Furthermore, there is very little possibility of the release of HCl into food items from CPH_1 blend film packaging because HCl underwent chemical bonding with the CMC/PVA composite or maximum unreacted HCl may have been driven away during casting. So, the proposed CPH_1 film could be considered a safe food-packaging material.

DSC Analysis

DSC analysis is often used as criterion for determining the miscibility of a solution. The glass-transition temperature (T_g), melting temperature (T_m), crystallinity, and melting enthalpies of a polymer or other material are determined by DSC. DSC thermograms of the pure CMC, pure PVA, and CP and CPH films are shown in Figures 9 and 10.

The pure CMC thermogram showed a sharp and broad endothermic peak at 83.33°C; it indicated T_g because of its crystalline structure. The pure PVA thermogram showed a small peak at 44.91°C due to the loss of water or moisture. A strong peak observed at 226.81°C with an enthalpy change (ΔH) of 69.55 J/

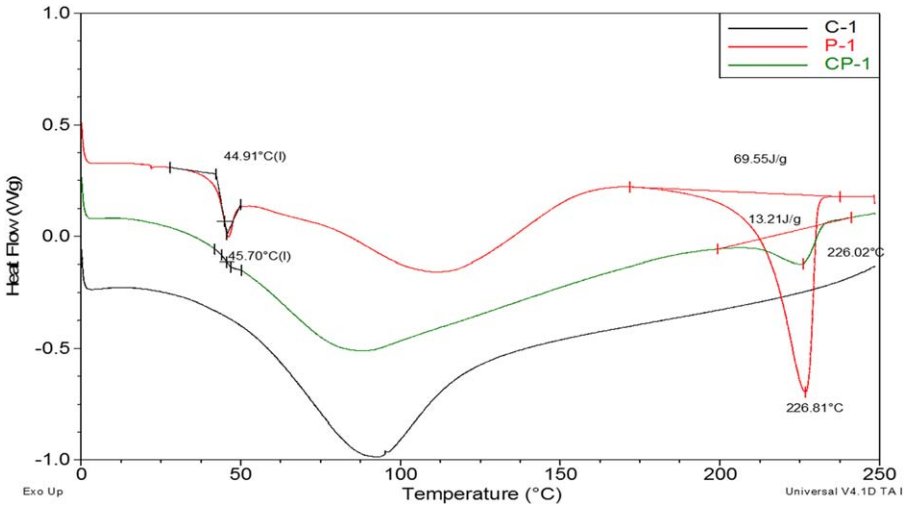


Figure 9. DSC curves of the pure CMC (C-1), pure PVA (P-1), and 30:70 CMC/PVA blend film (CP-1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

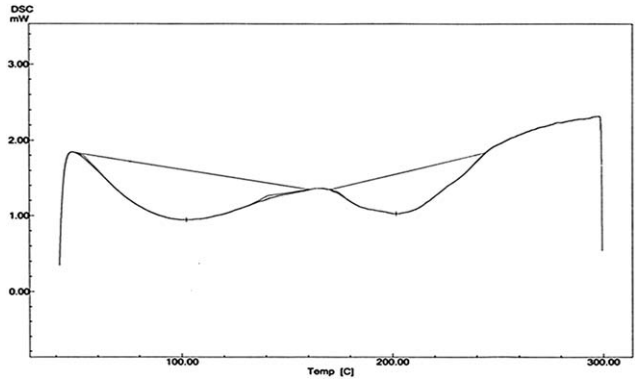


Figure 10. DSC of CPH_1.

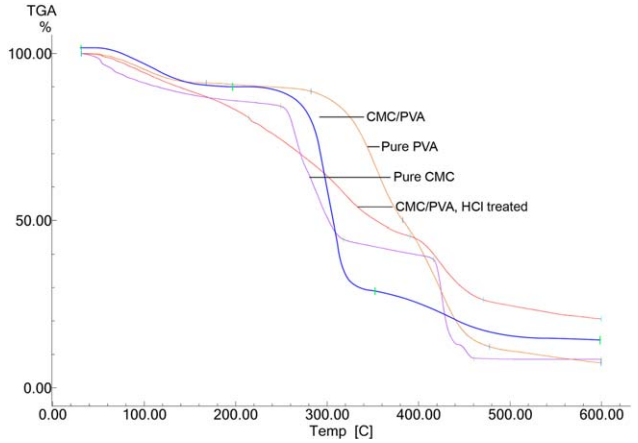


Figure 11. TGA curves for the pure CMC, pure PVA, CP with 30:70 CMC/PVA, and CPH_1 films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

g indicated T_m of PVA. A strong and narrow exothermic peak observed at 202.28°C represented T_g and also indicated the crystallization transition.

The CP film showed a small peak at 44.76°C; this indicated the loss of water molecules. A strong endothermic peak at 225.26°C with a ΔH of 36.62 J/g indicated the melting transition, which was very close to that of pure PVA; this implied that no chemical reaction occurred between CMC and PVA.

The T_g of the amorphous fraction and the T_m of CPH_1 are shown in Figure 10. CPH_1 exhibited a sharp endothermic peak (typical of a semicrystalline polymeric system) in the range 53.43–140.69°C, with the highest peak at 102.06°C and a ΔH of 116.49 J/g; this indicated T_g. Another endothermic peak observed in the range 173.52–239.33°C, with the highest peak at 201.43°C and a ΔH of 64.61 j/g, indicated the melting transition of the film. The T_m of CPH_1 blend was 201.43°C, that is, 23.83°C lower than that of CP. The decreased melting point indicated that the interaction between CMC and PVA weakened the interaction between the PVA chains and hindered the crystallization of PVA. The difference in melting point for CPH_1 was also supported by the occurrence of chemical modification in the structure of the film; that is, CMC and PVA reacted with each other and caused a lower degree of crystallinity (Table I).

TGA

The TGA thermogram of the pure CMC, pure PVA, CP, and CPH_1 films are shown in Figure 11. In the thermal degradation studies of pure CMC, four distinct steps were observed that showed the consecutive weight loss. The first step (from 20 to 246.57°C) represented the elimination of moisture and water, which was hydrogen-bonded with hydrophilic —OH and $—COO^-$ groups. The maximum degradation took place in the second step (from 246.57 to 315.43°C) and may have been due to the rupture of —COO groups and C—C bonds of CMC to form CO_2.[38] The third step of degradation (from 315.43 to 414.87°C) was followed by a further smaller weight loss (6.10%), which was due to the breaking of moderately stronger bonds. The fourth step of degradation (from 414.87 to 459.15°C) was predominantly the characteristic decomposition of CMC, which occurred by the breaking of the backbone.[39]

Table I. Comparative DSC Results for the CMC, PVA, CP, and CPH_1 Films

Film type	T_g (°C)	T_m (°C)
CMC	83.33	None
PVA	202.28	226.81
CP	None	225.26
CPH_1	102.06	201.43

In the TGA thermogram of pure PVA, three weight loss steps were observed. The initial weight loss (ca. 11.4%) within the temperature range 33.0–283.21°C was associated with the elimination of moisture and water. Steps 2 and 3 were the degradation steps. The maximum degradation (ca. 76.38%) was observed in the range 283.21–477.43°C and was due to the characteristic decomposition of PVA (cracking of PVA).[40,41]

The thermogram of CP showed three distinct zones. The first one, from 28.92 to 190.00°C, represented the elimination of moisture and water (ca. 10.90%). On the other hand, the rest of the zones represented the degradation of the film. The maximum degradation (ca. 57%) occurred in the second zone from 190 to 352°C for the decomposition of the film. In the third zone, from 352 to 600°C, a slow degradation of about 13.6% was observed. It was due to the moderately stronger bond breaking of the polymer backbone. Meanwhile, after 480°C, the curve became flat; this indicated that inorganic residue remained.

In the comparative analysis of the TGA results of the CP and CPH_1 films, as shown in Table II, we observed that for CP, within the temperature range 200–352°C, a maximum degradation of 57% was observed, whereas in the case of CPH_1, within the temperature range 214.24–390.75°C, about 35.46% was degraded. So, the weight loss of CP was larger than that of CPH_1 under 300°C (Figure 11 and Table II). The total weight loss of CP (81.50%) was also larger than that of the CPH_1 blend (79.46%). This indicated that the thermal stability of the HCl-treated film was higher than that of the film without acid treatment.

Table II. Comparative TGA Results for the CP and CPH_1 Films

CP		CPH_1	
Temperature range (°C)	Weight loss (%)	Temperature range (°C)	Weight loss (%)
28.92-190.00	10.90	30.92-214.24	19.25
190.00-352	57.00	214.24-390.75	35.46
352.00-600.00	13.60	390.75-471.06	19.05
		471.06-600.00	5.70
Total	81.50		79.46

The TGA curve of the CPH_1 blend showed a slow but gradual decrease in weight loss in the range 30.92–600°C with no stepwise weight loss or degradation like other films. The total weight loss of the CPH_1 blend film from 30.92 to 600°C, with a hump at 400°C, was observed as 79.46%. All of the thermogravimetric curves provided that at a temperature of higher than 450°C, all of the curves became flat; this indicated that mainly inorganic residues remained. Because the CPH_1 blend film degraded almost in a single step and exhibited the lowest weight loss among other films, this suggested a higher thermal stability and the occurrence of crosslinking between CMC and PVA.

CONCLUSIONS

CMC/PVA blends of various compositions (weight percentages) were prepared by solution casting with and without hydrochloric acid. The physical properties, including the mechanical properties, water uptake, and solubility in water, of both types of blend films were investigated by different techniques. The films were also characterized by ATR–FTIR spectroscopy, DSC, and TGA. The results show that in the presence of hydrochloric acid, chemical modifications occurred between CMC and PVA. The blends prepared without hydrochloric acid exhibited brittleness, a strong water absorption capacity, a higher water solubility, and low mechanical properties. So, they could not be considered as packaging materials, although the films prepared by the treatment with HCl of various compositions of CMC/PVA showed low water uptakes, minimum water solubility, optimum mechanical properties, and biodegradability. Because of the physicochemical characteristics of all of the compositions of the CMC/PVA/HCl blends, CPH_1 was optimized as a better biodegradable packaging material. As far as we know, no specific research about the CMC/PVA/HCl blend has been reported before now. In comparison to related works, our optimized film can be considered as an exceptional biodegradable packaging material in all respects.

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