Fabrication and characterization of polyvinyl alcohol/carboxymethyl cellulose/titanium dioxide degradable composite films: an RSM study

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Keywords: composite film, Packaging, PVA, RSM, characterization

Abstract
The main aim of the current study was to design and fabricate biodegradable antibacterial composite films composed of polyvinyl alcohol/carboxymethyl cellulose/titanium dioxide (PVA/CMC/TiO₂) with appropriate potential for packaging applications. The process was designed using the response surface methodology (RSM) via the Design Expert software. PVA was chosen as the main portion of the film, and the weight percent of CMC and TiO₂ were selected as the important parameters affecting the mechanical properties, degradability, and water vapor permeability (WVP) of the prepared samples. Statistical analysis confirmed that software presented quadratic equations could predict the governed relations between process parameters and selected responses properly. These equations showed that adding CMC and TiO₂ improved mechanical and barrier properties of the pure PVA matrix, while the degradability and WVP decreased due to uniform dispersion of TiO₂ into the matrix. However, further adding of CMC and TiO₂ reduced mechanical and barrier properties probably due to agglomeration of nanoparticles and embrittlement of the matrix. Furthermore, significant antibacterial property against Escherichia coli was observed via the disk diffusion method for the composite films due to presence of TiO₂. Overall, the current study findings support the potential of PVA/CMC/TiO₂ compounding for fabrication of active biodegradable packaging films.

1. Introduction

Enclosing or protection of products for distribution, storage, sale, and use is one of the most important issues in food manufacturing processes. The proper packaging should maintain the quality of food products from storage and transportation until final use [1, 2]. Food packaging materials are usually made of petroleum-based plastics due to their good mechanical properties, processability and their excellent barrier against water vapor; however, due to their non-biodegradability, severe environmental problems raise all over the world. Hence, several research works have been focused on the development of food packaging materials using biodegradable polymers degrading easily in the environment [3–5].

Rapid biodegradability, non-toxicity, biocompatibility with other biopolymers, harmless interaction with food, and in some cases, their intrinsic antimicrobial properties are the advantages of biopolymers compared to those obtained from the petroleum industry [6, 7]. Biodegradable polymers can be categorized into natural and synthetic ones; the former such as chitin, chitosan, starch, gelatin, and cellulose are obtained from natural sources, and the latter such as polyvinyl alcohol (PVA) and polylactic acid (PLA) require chemical synthesis [8]. Nevertheless, degradable polymers have poor mechanical strength and barrier property against water vapor and most of them are expensive with poor processability; therefore, attempts have been made to overcome these drawbacks usually by blending as well as using nanoparticles [3].

Various nanomaterials have been used for food packaging films as functional additives, including silver nanoparticle (Ag), nano-clay, nano-zinc oxide (ZnO), titanium dioxide (TiO₂), carbon nanotubes (CNTs),
cellulose nano-whiskers, and starch nano-crystals [9, 10]. The use of nanoparticles with intrinsic antimicrobial properties has opened an interesting topic among researchers, as active food packaging that prolonged the preservation time as well as the quality of the food [11].

Kanatt et al. [12] prepared active films composed of chitosan, PVA, aqueous mint extract (ME), and pomegranate peel extract (PE). They investigated the effect of the extracts on the physical, mechanical, antimicrobial, and antioxidant properties of the films and showed that addition of ME/PE improved the tensile strength of the samples without affecting their puncture strength as well as permeability characteristics. The films also exhibited antibacterial activity against Staphylococcus aureus and Bacillus cereus due to presence of ME/PE. Finally, they suggested that chitosan/PE film containing ME/PE could be used to develop active food packaging materials. Taghizadeh et al. [13] prepared PVA/starch/carboxymethyl cellulose composite films by the solution casting method at three different loadings of carboxymethyl cellulose (CMC) and starch. The effects of the CMC addition on some physical properties of the prepared samples were investigated, and it was found that proper interaction between the three parts obtained with addition of 20 wt% CMC improved the tensile strength and elongation at break. Moreover, the thermal stability of PVA/starch/CMC blend was higher than that of PVA/starch, suggesting that the addition of CMC improved the thermal stability of PVA/starch blend. In our previous works, the effect of addition of gelatin and graphene oxide [14] as well as gelatin and silica [15] on improving the properties of starch-based nanocomposite films was studied. It was reported that there was good interaction between starch, gelatin, and nanoparticles. Furthermore, the presence of gelatin and nanoparticles improved mechanical, water vapor barrier, and thermal properties of the starch. Moreover, the presence of silica brought significant antibacterial properties against Escherichia coli and Staphylococcus aureus.

In the current study, preparation and characterization of PVA/CMC/TiO2 nanocomposite films were reported. The fabrication process was designed using the response surface methodology (RSM) via the Design-Expert 7.0 software by defining CMC and TiO2 wt% as the important parameters affecting the various properties of the final nanocomposite films. The potential of the selected compounding as a proper candidate to produce packaging films was confirmed.

2. Experimental

2.1. Materials
Polyvinyl alcohol (PVA, Merck, with average Mw of 145 000 g mol\(^{-1}\)), carboxymethyl cellulose sodium salt (CMC, Daejung, with average Mw of 250 000 g mol\(^{-1}\)), titanium dioxide (US Research Nanomaterials, Inc. with an average size of 20 nm), citric acid (Merck), and glycerin (Sigma Aldrich) were used to fabricate the samples.

2.2. Design of experiment and fabrication of samples
The Design Expert Software 7.0 was applied for the statistical design of experiments, data analysis, and process optimization [16–18]. The central composite design (CCD) and response surface methodology (RSM) were used to optimize the three most important operating variables, namely mechanical properties, degradation behavior, and water vapor permeability (WVP). Thirteen experiments were conducted to determine the governing relations between process parameters, namely CMC and TiO2 wt% and the defined responses, namely tensile strength, elongation at break, degradation percent, and water vapor permeability. The selected ranges for CMC and TiO2 were 0–30 and 0–3 wt%, respectively. Table 1 shows the CCD design fabrication conditions, including 13 runs (9 + 4 additional experimental trials as replicates of the central point) and the obtained experimental results at each assay. In this table, the independent variables levels are presented in terms of the original unit of measurement (wt%) at coded levels (in parentheses), including −1 (minimum), 0 (central), and +1 (maximum).

Each defined response was related to the process parameters via a quadratic equation according to equation (1) to be able to predict the optimal conditions for fabrication of composite films.

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_iX_i^2 + \sum_{i<j=1}^{k} \beta_{ij}X_iX_j + \ldots + \varepsilon
\]  

(1)

The interaction between the process variables and the responses was graphically and statistically investigated by drawing the relevant three-dimensional plots and using analysis of variance (ANOVA), respectively. The quality of the fit polynomial model was investigated by the coefficient of determination (\( R^2 \)) and the Fisher's F-test, while the model terms were evaluated by the P-value (probability) with 95% confidence level [16].

Total weight of the matrix was fixed at 5 g (dried polymer: PVA + CMC), and the percent of TiO2 was calculated according to the weight of the matrix. The composite films were fabricated via the solution casting method due to the conditions in presented table 1. The prescribed amount of TiO2 was dispersed in 50 ml distilled water by 20 min sonication, the PVA was added to the system, and it stirred at 50 °C for 2 h. The CMC
was dissolved in 50 ml distilled water separately under 2 h mild stirring at 50 °C. The obtained homogenous solution was added to the PVA/TiO$_2$ mixture and stirred for 2 h at ambient temperature, while citric acid and glycerin were gradually introduced as a crosslinker and a plasticizer, respectively. The mixture was sonicated for 30 min, casted on polyethylene Petri dishes, and cured in the oven at 45 °C for 48 h. The analyses were performed at the temperature and relative humidity of 25 ± 2 °C and 40%–45%, respectively.

### 2.3. Characterization

#### 2.3.1. Fourier transform infrared spectroscopy, FT-IR

FT-IR spectra from matrix, TiO$_2$ powder, and composite were obtained using a Perkin-Elmer 1710 Spectrometer in the wavenumber of 4000–500 cm$^{-1}$ with scan rate of 4 cm$^{-1}$ at ambient temperature to investigate the interaction between three compounds.

#### 2.3.2. X-ray diffraction, XRD

XRD patterns from the matrix, TiO$_2$ powder, and composite were obtained using a X’Pert PRO equipment at operating condition of 40 kV and 40 mA. The radiation was generated from a Cu-Ka ($\lambda = 0.156$ nm) source with scan rate of 1° per step.

#### 2.3.3. Scanning electron microscope, SEM

SEM images were obtained from fractured cross-section of the pure matrix and composite to investigate the interaction between polymer and nanoparticles as well as from the surface of degraded composite film to investigate the degradation behavior of the samples. The images were taken by high-vacuum microscope (Quanta, US) at an accelerating voltage of 10–20 kV after gold coating the target surface of the sample.

#### 2.3.4. Mechanical test

Mechanical properties of the composite films i.e. tensile strength and elongation at break were analyzed by using GOTECH Al-3000 (Taiwan) instrument. The sample was cut into rectangular pieces of 10 mm × 120 mm with thickness of 50 ± 10 μm. The tensile speed was 5 mm/min under the load of 5 N. The stress-strain curves were drawn and the stress and strain at breaking point were reported as tensile stress (MPa) and elongation at break (%), respectively.

#### 2.3.5. Water vapor permeability, WVP

The gained weight of the samples was measured as criteria for WVP as described in our previous works [14, 15]. The falcon tube was semi filled with dried silica gel; its door was sealed with prepared film, weighted ($m_0$), and put into desiccator with relative humidity of 40%–45%. The tube was weighted hourly ($m_1$) for 14 h and its weight changes ($m_1-m_0$) versus time ($t$) was drawn. The slope of the curve ($\Delta m/t$, g/h) was calculated by fitting a linear curve and divided by the surface are of the water vapor exposed film ($A = 0.000 615$ m$^2$). The obtained data was multiplied by the sample thickness and reported as film permeability (g/s/m).

### Table 1. The software suggested values for S/G wt ratio and SiO$_2$ wt% and the measured responses.

| Run | A CMC wt% | B TiO$_2$ wt% | Tensile Strength (MPa) | Elongation (%) | Degradation (%) | WVP (g/s/m×10$^8$) |
|-----|-----------|----------------|------------------------|---------------|----------------|-------------------|
| 1   | 15 (0)    | 0 (-1)         | 25.21                  | 215.36        | 19.85          | 4.21              |
| 2   | 0 (-1)    | 3 (+1)         | 21.3                   | 323.36        | 15.53          | 4.28              |
| 3   | 15 (0)    | 1.5 (0)        | 33.5                   | 270.54        | 15.47          | 3.59              |
| 4   | 30 (+1)   | 3 (+1)         | 16.5                   | 132.69        | 12.74          | 4.26              |
| 5   | 0 (-1)    | 1.5 (0)        | 31.5                   | 355.21        | 17.21          | 4.11              |
| 6   | 15 (0)    | 1.5 (0)        | 33.5                   | 270.54        | 15.32          | 3.59              |
| 7   | 15 (0)    | 1.5 (0)        | 33.5                   | 270.54        | 15.32          | 3.59              |
| 8   | 30 (+1)   | 1.5 (0)        | 28.45                  | 169.21        | 14.2           | 3.97              |
| 9   | 15 (0)    | 1.5 (0)        | 33.5                   | 270.54        | 15.32          | 3.59              |
| 10  | 30 (+1)   | 0 (-1)         | 22.2                   | 120.64        | 18.52          | 4.42              |
| 11  | 15 (0)    | 1.5 (0)        | 33.5                   | 270.54        | 15.32          | 3.59              |
| 12  | 0 (-1)    | 0 (-1)         | 23.2                   | 291.23        | 22.45          | 4.85              |
| 13  | 15 (0)    | 3 (+1)         | 21.1                   | 227.36        | 13.94          | 3.93              |
2.3.6. Degradation test
Soil burial test was carried to investigate the degradation of the prepared samples [14, 15]. The sample was cut by 5 cm × 5 cm, weighted (m₀), and buried under the normal agricultural soil at temperature of 25 ± 2 ºC. It was weighted weekly (m₁) and its weight loss reported as sample degradation percent (equation (2)).

\[
D (\%) = \frac{m_0 - m_1}{m_0} \times 100
\] (2)

2.3.7. Antimicrobial test
Antimicrobial activity test was done by using the agar disk diffusion method against *Escherichia coli* as gram negative bacteria and *Staphylococcus aureus* as gram positive. Ethanol sterilized disks cut from film (diameter of 6 mm) was placed on the Petri dishes containing Mueller–Hinton agar previously spread with 0.1 ml of each inoculum. The bacterial culture concentration in the inoculum was 10⁶ CFU1 and was used as control samples.

2.3.8. Degradation test
Soil burial test was carried to investigate the degradation of the prepared samples [14, 15]. The sample was cut by 5 cm × 5 cm, weighted (m₀), and buried under the normal agricultural soil at temperature of 25 ± 2 ºC. It was weighted weekly (m₁) and its weight loss reported as sample degradation percent (equation (2)).

\[
D (\%) = \frac{m_0 - m_1}{m_0} \times 100
\] (2)

3. Results and discussion

3.1. Statistical analysis
The quadratic relationships between two variables i.e. CMC wt% (A) and TiO₂ wt% (B) and four important process responses (tensile strength, elongation at break, degradation, and WVP) for the composite film fabrication process were extracted from the software and provided in table 2. Furthermore, the relevant ANOVA data, which are useful to assess the models provided in this table. As can be seen, the relations consist of the sum of a constant, two first-order effects (terms in A and B), one interaction effect (AB), and two second-order effects (A² and B²) according to equation (1).

Data presented in table 2 demonstrate that all the models were significant at the 5% confidence level; since P-values were lower than 0.05. The lack of fit (LOF) F-test describes the variation of the data around the fitted model, and if the model does not fit the data well, this will be significant [16]. The large P-values for lack of fit (>0.05) presented in table 2 (PLOF) show that the F-statistic was insignificant, implying the significant model correlation between the variables and the process responses.

The R² coefficient gives the proportion of the total variation in the response predicted by the model, indicating the ratio of sum of squares due to regression (SSR) to total sum of squares (SST). In other words, it is a statistical measure of how close the data are to the fitted regression line and a high R² coefficient ensures a satisfactory adjustment of the quadratic model to the experimental data. Furthermore, a high R² value, close to 1, is desirable, and reasonable agreement with adjusted R² is necessary [20]. Therefore, due to reported R² and adj-R² (table 2), it can be concluded that the quadratic model appropriately predicts the relation between the process parameters and the relevant responses.

Adequate precision (AP) compares the range of the predicted values at the design points to the average prediction error, and ratios greater than 4 indicate adequate model discrimination [21]. As table 2 shows, AP values higher than 4 for all the responses confirm that all the predicted models can be used to navigate the design space defined by the CCD. In this regard, the predicted versus actual values plots (figure 1) could be useful for more adjudication of the model satisfactoriness. As can be seen, there is adequate agreement between real data and those obtained from the models.

The coefficient of variance (CV) is the ratio of the standard error of estimate to the mean value of the observed response and defines reproducibility of the model. A model normally can be considered reproducible if its CV is not greater than 10% [21]; therefore, all the models could be considered reproducible due to reported CV (table 2).

3.2. Regression model equations analysis
The governing relations between process parameters and selected responses presented in table 2 are graphically illustrated as response surface plots in figure 2. For tensile strength and WVP, the graphs are dome shape implying that the optimum conditions for those responses are attributed to CMC and TiO₂ wt% in the design space, while for elongation at break and degradation, they are saddle shape.

1 Colony-forming unit.
Table 2. ANOVA results.

| Response                  | Final equation in terms of code factors | P      | PLOF | $R^2$   | Adj.$R^2$ | AP        | CV (%) |
|---------------------------|----------------------------------------|--------|------|---------|-----------|-----------|--------|
| Tensile Strength (MPa)    | $33.39 - 1.48A - 1.95B - 0.95AB - 2.99A^2 - 9.81B^2$ | <0.0001 | 1.59 | 0.9956  | 0.9925    | 47.584    | 8.78   |
| Elongation (%)            | $272.05 - 91.21A + 9.36B - 5.02AB - 7.66A^2 - 48.51B^2$ | <0.0001 | 1.06 | 0.9973  | 0.9954    | 72.252    | 1.95   |
| Degradation (%)           | $15.39 - 1.62A - 3.10B + 0.28AB + 0.36A^2 + 1.55B^2$ | <0.0001 | 0.82 | 0.9964  | 0.9938    | 67.127    | 1.27   |
| WVP (g/s/m × 10^9)        | $3.60 - 0.098A - 0.17B + 0.10AB + 0.42A^2 + 0.45B^2$ | <0.0001 | 1.76 | 0.9930  | 0.9980    | 41.056    | 1.1    |
With increasing CMC portion in the matrix, the tensile strength increased then decreased. The increment could be related to formation of hydrogen bonds between the carboxyl group of CMC and the hydroxyl group of PVA [22], making a strong network in the matrix and causing it to bear more stress during the tensile test. As figure 2(a) clearly shows, further increment of CMC portion has made the matrix brittle; therefore, it cannot bear more stress and breaks under lower applied force. With introducing CMC into PVA, the elongation at break decreased as illustrated in figure 2(b), implying the matrix has become more brittle and its elasticity decreased.

**Figure 1.** Predicted versus actual values plot for responses: (a) tensile strength (MPa), (b) elongation at break (%), (c) degradation (%), and (d) WVP (g/s/m × 10⁸).

**Figure 2.** Response surface plot for responses: (a) tensile strength (MPa), (b) elongation at break (%), (c) degradation (%), and (d) WVP (g/s/m × 10⁸) as function of CMC and TiO₂ wt%.
Blending PVA with CMC slightly decreased the degradation percent of the matrix that can be related to its enforcing effect via forming strong polymeric networks. However, its effect on the degradation is not considerable due to its inherent degradability. Two mechanisms could be imaginable to prevent passing water molecule through the matrix: interconnected formed polymeric networks between carboxyl groups of CMC and hydroxyl groups of PVA acting as a barrier against passing of water molecule, and trapping of water molecules by forming hydrogen bonds with free hydroxyl groups of PVA. At a lower amount of CMC, both barrier and trapping properties help water vapor permeability of the matrix to decrease while at its higher amounts, the permeability increases as clearly observable in figure 2(d), due to reduction of PVA free hydroxyl groups trapping water molecules.

Several studies have confirmed that proper dispersion of nanoparticles into polymer matrix and their good compatibility improve physical, mechanical, barrier, and thermal properties of the matrix [23–25]. As figure 2(a) illustrates, tensile strength of the matrix increased by introducing TiO₂ up to approximately 1.5 wt% then decreased. Improvement of the tensile strength could be related to proper dispersion of nanoparticles into the matrix and their good interaction, causing better stress transfer between matrix and TiO₂ and consequently bearing more applied force by the sample. Reduction of the tensile strength is due to agglomeration of the nanoparticles and consequently formation of stress concentration points in the matrix acting as breakpoints. The behavior of the elongation at break with introducing TiO₂ is similar to the tensile strength trend where increased with increasing nanoparticles up to 1.5 wt% due to formation of strong networks between the polymer chains and TiO₂ followed by reduction due to agglomeration of nanoparticles. As figure 1(c) demonstrates, the effect of TiO₂ on degradation of composite films was more dominant than CMC effect where it decreased as nanoparticles were introduced into the matrix. This reduction could be explained by two mechanisms: one is the formation of strong networks into the matrix due to proper dispersion and interaction between two phases keeping the integrity of the film during degradation process, and the second is the reduction of water penetration into the matrix as a major destructive factor of the sample. Figure 1(d) clearly shows the reduction of water permeability of the sample in the presence of the TiO₂. It was confirmed that uniform dispersion of nanoparticles could decrease water vapor and gas permeation through polymeric films by prolonging the pathway of molecules due to formation of barrier sites inside the sample [26]. Further increase in TiO₂ portion in the composite reduced barrier properties due to agglomeration of nanoparticles and consequently loss of their uniformity into the matrix.

3.3. Optimization, validation, and sample characterization

All the prepared composite films might have potential to be used as packaging films; however, it is suitable to introduce the best candidate for the claimed application. Therefore, optimization was carried out using the RSM software. Since it is desirable to have films with maximum tensile strength and minimum water vapor permeability, numerical optimization was carried out by setting tensile strength and WVP at their maximum and minimum possible value and the other two responses kept in their ranges. The optimum conditions were as CMC wt% of 14.85 and TiO₂ wt% of 1.52. Furthermore, the predicted responses were 33.37 MPa, 273.03%, 15.37%, and 3.60 × 10⁻⁸ g/s/m for tensile strength, elongation at break, degradation percent, and water vapor permeability, respectively.

Validation experimental run was conducted using the optimum conditions in thrice, and the obtained average values of tensile strength, elongation at break, degradation, and WVP were 31.03 MPa, 262.1%, 13.98%, and 3.36 × 10⁻⁸ g/s/m, respectively. Compared to those predicted ones, there is an error of less than 9%; therefore, there is good agreement between the experimental values and the predicted ones based on the model. It is also pertinent to mention that the optimized tensile strength and elongation at break obtained in this study for the composite film are remarkably comparable to those for conventional polyethylene-based packaging films with the prominence that here significant degradability of the films is available [27].

On the other side, the obtained results for the optimum sample have good agreement with the results of the other research groups that used similar composition. Cazon et al [28] reported 34.63 MPa, 49.89%, and 5.63 × 10⁻⁸ g/s/m, respectively for the tensile strength, elongation at break, and WVP of bacterial cellulose/glycerol/PVA composite. In on other research work [29] tensile strength, elongation at break, and WVP were reported as 10.34 MPa, 39.14%, and 37.90 × 10⁻⁸ g/s/m, respectively for CMC/PVA blend films. Tensile strength and WVP were reported by Muppalla et al [30] as 100 MPa and 0.213 × 10⁻⁸ g/s/m, respectively for cCMC/PVA/clove oil films. Wu et al [31] reported that starch/PVA/graphene oxide composite films can show tensile strength, elongation at break, and WVP as 25.28 MPa, 184.03%, and 5.25 × 10⁻⁸ g/s/m, respectively.

3.3.1. Structural and morphological study

Figure 3 presents the FT-IR spectra of the matrix (PVA/CMC), TiO₂, and optimum composite film. It is reported that the FT-IR spectrum of the PVA film shows characteristic peaks as follows: the band at the range of
3100–3500 cm⁻¹ assigned to -OH stretching, the bands at approximately 2940 cm⁻¹, 2907 cm⁻¹ and 1425 cm⁻¹ attributed to -CH2- asymmetric stretching and symmetrical bending, the bands at approximately 1142 and 1088 cm⁻¹ corresponded to C–O stretching of the crystalline and amorphous area of PVA [32]. The FT-IR spectrum of pure CMC film shows a broad absorption peak at 3354–3454 cm⁻¹ owing to the stretching frequency of the hydroxyl groups and the absorption peak at 2914 cm⁻¹ attributed to the stretching vibrations of the C–H bonds. Two strong peaks appeared at 1462 and 1603 cm⁻¹ are assigned to the symmetric and asymmetric stretching vibrations of the carboxylate groups, the intense absorption peak at 1318 cm⁻¹ corresponded to –OH bending vibrations, and the bands at 1172, 1062 and 1025 cm⁻¹ belonged to the C–O stretching vibrations (C–O–C), which are characteristics of the polysaccharide skeleton [33]. The peaks appeared in the matrix spectrum (figure 3(a)) are similar to those already mentioned for PVA and CMC; in other words, simple physical blending without any chemical bonds occurred between the two polymers. Furthermore, in composite FT-IR spectrum (figure 3(c)), both matrix and TiO2 (figure 3(b)) peaks could be observable with slight displacement, confirming the existence of the three compounds in the sample and the physical blending without any chemical bonds between them.
It is reported that neat PVA film shows a major reflection at $2\theta = 19.4^\circ$ [34] and neat CMC film shows a relatively broad diffraction peak with a maximum appearing at nearly $2\theta = 20^\circ$ both indicating a semicrystalline structure [35]. Furthermore, TiO$_2$ powder reveals dominant peaks at $2\theta = 25.35^\circ$ and $26.68^\circ$ and weaker peaks around $2\theta = 37.8^\circ$, $48.12^\circ$, $53.97^\circ$, $55.14^\circ$, and $62.78^\circ$ [35]. The maximum sharp peak for the TiO$_2$ nanoparticle powder at $2\theta = 25.35^\circ$ indicates a crystalline structure for the nanoparticle powder with its crystallite size calculated from Scherrer’s equal to 26.67 nm [35] that has good agreement with particle size of the TiO$_2$ used in the current study. As figure 4 illustrates, the matrix and TiO$_2$ XRD spectra show diffraction peaks similar to those already discussed [34, 35], and these peaks are kept in the composite spectrum (figure 4(c)) confirming that three components are available in the final sample.

To investigate the dispersion of nanoparticles into the matrix and their interaction, SEM images were taken from cross-section of the matrix and optimum composite (figure 5). As figure 5(a) shows, no phase separation is observable in the SEM image of the matrix implying that there is good compatibility between PVA and CMC. This good compatibility is kept in the composite SEM image (figure 5(b)). Furthermore, good compatibility between nanoparticles, polymer phase and uniform dispersion of TiO$_2$ into the matrix is also observable in the SEM image improving the physical and mechanical properties of the film as already observed in mechanical and permeability tests.
SEM images were also used for further investigation of degradability of the optimum composite film 6 weeks after test. As figure 6 shows, the uniformity of the surface has been demolished and several defects could be detectable on it, confirming that significant degradation occurred for the sample 6 weeks after test.

3.3.2. Thermal stability
Thermal properties is one the important issues for packaging film; therefore, thermal degradation of the matrix and composites with two different TiO\textsubscript{2} wt\% were investigated and presented in figure 7. It is reported that pure PVA shows three lose weight regions: the first one at 50–170 °C that can be assigned to evaporation of residual solvents, mainly the trapped water. The second drop at 200–350 °C corresponds to the elimination reaction of water. The third one at 400–550 °C that is associated with further decomposition of polymer residues to yield the carbon and hydrocarbons [35]. Three lose weight regions are also reported for CMC TGA curve as follows: the first one between 20 and 140 °C due to moisture evaporation, the second one between 220 and 305 °C due to decomposition of methylcellulose and decarboxylation of carboxyl groups, and the last one between 305 and 600 °C corresponding to the final decomposition [36]. As illustrated, the TGA curve of the matrix shows three weight loss regions; one between 70 and 200 °C, the next one between 200 and 350 °C, and the last one between 350 and 600 °C corresponding to decomposition of both PVA and CMC. These three loss weight regions are also observable in composites TGA curves with slight displacement where the dropping regions shifted to a higher temperature caused by reinforcing effect of the TiO\textsubscript{2} due to uniform dispersion and proper interaction between the nanoparticles and the matrix.
3.3.3 Antibacterial activity

Figure 8 shows the results of the antimicrobial test performed against *S. aureus* and *E. coli* for pure matrix, chloramphenicol soaked paper, and composite film with various TiO$_2$ concentration. As can be seen, inhibition zones appeared for all composite samples against *E. coli* and they increased with increasing TiO$_2$ portion in the matrix, while they did not appear for pure matrix, confirming the positive effect of the TiO$_2$ for bringing antibacterial properties for the pure matrix. However, the inhibition zones were not significant for *S. aureus* that could be owing to the higher resistance of gram positive microorganisms to TiO$_2$. Othman et al [37] also investigated the antibacterial properties of TiO$_2$ coated polyethylene (PE) for its potential as active food packaging and showed the presence of TiO$_2$ as coating on the surface of conventional PE-based film bringing significant antibacterial properties against *E. coli*. Zhang et al [38] also showed incorporation of TiO$_2$ into chitosan film enhanced the antimicrobial activity of the film against *E. coli*.

4. Conclusion

Fabrication and characterization of the composite film composed of PVA/CMC/TiO$_2$ were reported in this study. Fabrication process was designed using RSM and central composite design (CCD) via the Design Expert software. PVA was selected as the main part of the matrix and the effect of adding CMC and TiO$_2$ on improving the properties of the final composite films investigated. The results showed that at a lower amount of CMC and TiO$_2$, the mechanical and barrier properties of the matrix improved due to formation of hydrogen bounds between hydroxyl groups of the PVA and carboxyl groups of the CMC as well as proper dispersion and good interaction between nanoparticles and matrix. Further addition of CMC and TiO$_2$ reduced the properties of the composite films due to embrittlement of the matrix caused by increase of the density of hydrogen bonds and agglomeration of the nanoparticles. Numerical optimization was carried out, optimum conditions for fabrication of the composite film were introduced, and the structural, thermal, and antibacterial properties of
the optimum sample were investigated. It was found that improved thermal properties of the matrix as well as significant antibacterial properties were obtained in the presence of the nanoparticles. Overall, the current study findings could be the first step to introduce the PVA/CMC/TiO₂ compounding as a suitable material to fabricate degradable composite films for packaging applications.

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