STUDY THE EFFECT OF TiO₂ NANOPARTICLES ON PHYSICAL PROPERTIES OF BIOPOLYMER BLEND

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Abstract. Chitosan (CH) / Poly (1-vinylpyrrolidone-co-vinyl acetate) (PVP-co-VAc) (7:3) blend [CH/(PVP-co-VAc)] reinforced with two types of nanoparticle of titanium oxide TiO₂ (type I & II) were prepared by solution casting method. The nanocomposites prepared with different concentrations (1, 2, 3.5, 5, 7.5, and 10) wt%. The tests carried out were AFM, FTIR, Tensile strength, Thermal conductivity measurement, and Weight gain. The results of the AFM test showed that the roughness of the surface decreased with the addition of a small amount of nanoparticles (1 wt.%) to the CH/(PVP-co-VAc) blend. FTIR results for blend film indicates a significant degree of composition between (PVP-co-VAc) and CH molecules. Nanocomposite films indicate that the composition among polymer blends and Nano are associated with changes in intensity, shape, and position of modes. The mechanical properties of chitosan were enhanced by the addition of TiO₂ nanoparticle with significant increases in tensile strength (from 47.87 MPa to 64.95 ~ 70 MPa). Because interfacial bonding and homogenous distribution between the nanoparticles and the blend were supportive of markedly improved mechanical strength. The results of thermal conductivity and water absorption showed that the highest values were achieved in the polymer blend (CH/ [PVP-co-VAc]), whereas its decrease with the increase of the nanoparticle incorporation.

Keywords: Natural polymer, nanocomposites, Physical properties.

1. Introduction

Chitosan (CH) is a natural carbohydrate biopolymer derived by deacetylation (DA) of chitin, a major component of the shells of a crustacean such as a crab, shrimp, and crawfish. After cellulose, chitin is the second most abundant natural biopolymer found in nature like cellulose; chitosan is a fiber. However, unlike plant fiber, chitosan possesses unique properties, including the ability to form films, optical structural characteristics and much more [1,2]. Chitosan shows first pledge for employ as a scaffold in tissue engineering, wound dressing applications, the antimicrobial therapy of textiles as well as water disinfection and microbial control [3-5]. Enforcement like food packaging and wound dressings frequently demand processing of chitosan into films. That is not straightforward as chitosan is insoluble in most common solvents (including water) but can be beat by dissolving chitosan in dilute aqueous acidic solutions [6]. It has been confirmed that aqueous acetic acid is one of the most suitable solvents in terms of the resulting film. The aim of this work is to report the effect of TiO₂ nanoparticle on the AFM, FTIR, tensile properties of polymer blend [CH/(PVP-co-VAc)] in addition to the thermal conductivity and weight gain. Maxing of two or more polymers is an important technique to improve the cost-effectiveness of commercial products. Chitosan films are brittle and not suitable for use in its dry state. Poly (1-vinylpyrrolidone-co-vinyl acetate) was select to blend with chitosan to enhance the mechanical properties with degradability of chitosan films [7].
2. Experimental Part

Chitosan (CH) with a degree of deacetylation of 85% and average molecular weight of 345,500 g·mol⁻¹, Titanium dioxide TiO₂ type (I) was about 65 nm, type (II) 42 nm anatase nanopowder, 99.7% trace metal basis, and Poly (1-vinylpyrrolidone-co-vinyl acetate) [PVP-co-VAc] with a molecular weight of ~5.0 × 10⁴ g. mol⁻¹ was obtained from Sigma-Aldrich.

2.1 Film Preparation

The blend of (CH) and (PVP-co-VAc) with the fixed ratio (7:3) have been prepared by dissolving 0.4 g of CH in 30 mL acetic acid (1% v/v), and 0.4 g of (PVP-co-VAc) in 10 mL acetic acid (1% v/v). The two solutions were put separately under continuous stirring for 2 h at room temperature, then mixed for about 1 hour. Finally, cast into a petri dish with 8 cm in diameter at room temperature for 24 h in a desiccator to ensure the removal of bubbles, after that the samples dried at 50 °C in an electric oven at for 6 h, then the films were peeled off. The nano-composites preparation was the same as the blend but adding the TiO₂ nanoparticles slowly to the (PVP-co-VAc) solution with continuous stirring for 30 min (by weight relative to CH) are 1, 2, 3.5, 5, 7.5 and 10 wt. % before mixing it with the CH solution to have proper distribution as tabulated in Table (1).

Table 1. The samples assigning and composition of blend{CP}named [CH+(PVP-co-VAc)] and the (TiO₂ [I], TiO₂ [II]) nanoparticles.

| Sample type       | CP | T1 | T2 | T3 | T4 | T5 | T6 | P1 | P2 | P3 | P4 | P5 | P6 |
|-------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Nano TiO₂ wt.%    | 0  | 1  | 2  | 3.5| 5  | 7.5| 10 | 1  | 2  | 3.5| 5  | 7.5| 10 |
| Type of NanTiO₂   | (I)| (I)| (I)| (I)| (I)| (I)| (I)| (II)| (II)| (II)| (II)| (II)| (II)|

2.2 Characterizations of films

1. Atomic Force Microscopy

Surface morphology and roughness of Titanium dioxide TiO₂ with two nanoparticle size (65& 42 nm), blend and nanocomposite films were studied by Atomic Force Microscope (AFM) analysis type (Angstrom AA3000, USA) for the measurement the roughness of the surface.

2. FTIR spectroscopy

FTIR characterization was done on the polymer electrolytes using the Shimadzu FT-IR 8000 series spectrum over the range of 400-4000 cm⁻¹ with resolution 4 of the spectra obtained at room temperature and recorded in the transmittance mode.
3. Tensile strength

The tensile strength of [CH/(PVP-co-VAc)] blend and nanocomposite specimens were characterized for their properties in the longitudinal direction by ASTM D882-02. The films were cut into slices with a dimension of 10 mm x 80 mm and with a thickness of 0.17 -0.24 mm. These specimens were all tested at a gauge length of 50 mm; tensile tests were performed at a crosshead speed of 5 mm min⁻¹.

4. Thermal conductivity

The thermal conductivity of the blend [CH/(PVP-co-VAc)] film and TiO₂ nanocomposite films was studied by using Lee’s disc method, homemade by the worker in material Laboratory Department of Physics. It’s designed to calculate the thermal conductivity of primarily thermal insulators such as. A thin, large surface area sample of 3 cm in diameter is used to determination of thermal conductivity to reach steady-state quickly.

5. Water absorption

Swelling behavior of the blend and CaCo₃ nanocomposite films was studied on rectangular specimens with (10×10 mm). The dry weight (W₁) of each sample was measured, and then the sample was immersed in distilled water of pH (6.5) at the time interval of 1, 2, and 3 h. The measurement was taken every 10 min, then, the sample was taken out, and the excess water on its surface was wiped with a filter paper. The swollen films eventually weighed. Weight gain of the samples was registered by periodic removal of the specimens from immersion and weighted. The weight gain % calculated, according to Coarse Aggregate AS per IS 2386 part 3, in Eq. 1 for blend and nanocomposite films.

\[
\text{Weight gain\%} = \left( \frac{W_2 - W_1}{W_1} \right) \times 100\% \quad \ldots \quad (1)
\]

where W₂ is the weight of the wet sample at time (t) after swelling, and W₁ is the weight of the dry sample before expanding.

3. Results and Discussion

3.1 Atomic Force Microscopy

The surface topology of the synthesize of Titanium dioxide TiO₂ with two nanoparticle size (65& 42 nm), blend and nanocomposite films have characterized by AFM. The result showed that the roughness of the surface decreased with the addition of the nanoparticles to the CH/(PVP-co-VAc) blend as shown in the Table (2) and Figure (1).

| Sample | Nano type | Ave. Grain size (nm) | Nano wt. % | Ave. Roughness (nm) |
|--------|-----------|----------------------|------------|---------------------|
| CP     | -         | -                    | 0 %        | 12.6                |
| T1     | TiO₂(I)   | 65                   | 1          | 0.87                |
| T6     | TiO₂(I)   | 65                   | 10         | 18                  |
| P1     | TiO₂(II)  | 42                   | 1          | 1.63                |
| P6     | TiO₂(II)  | 42                   | 10         | 9.2                 |
3.2 FTIR Spectroscopy

Figure (2) shows the FTIR spectra of raw materials, as for CH and (PVP-co-VAc) the prominent peak observed at 3431.84 cm\(^{-1}\) corresponds to the intermolecular hydrogen bonding. A peak obtained at 2925.53 cm\(^{-1}\), 2855.66 cm\(^{-1}\) indicates the asymmetric and symmetric C-H stretching in CH\(_2\) respectively. A peak observed at 1718.20 cm\(^{-1}\), 1623.22 cm\(^{-1}\) indicates the presence of C=O is stretching in secondary amide and N-H bending, respectively. These peaks confirm the blending of (PVP-co-VAc) and chitosan [8]. From Figure (2) the FTIR spectrum of TiO\(_2\) nanoparticles it can noticed clearly that the bands for Ti-O and Ti-O-Ti are present in the 800 - 400 cm\(^{-1}\) region, the former observed in a higher wavenumber than the latter [9,10]. The peak about (800) cm\(^{-1}\) is allocated to a (Ti-O) vibration, where the oxygen atom is in the non-binding condition. The bands at 760 cm\(^{-1}\), 680 cm\(^{-1}\), 560 cm\(^{-1}\), 500 cm\(^{-1}\) and 468 cm\(^{-1}\) are associated to (Ti-O-Ti) vibrations [11,12]. These assignments of vibrational modes of the blend and nanocomposites bands were tabulated in Table (3).
Table 3. Assignments of vibrational modes and list of the observed peak for blend and nanocomposites.

| Assignments       | Wavenumbers (cm⁻¹) |
|-------------------|---------------------|
|                   | CP (0%)             | T4 (5%) | T6 (10%) | P4 (5%) | P6 (10%) |
| O-H & N-H         | 3298                | 3242    | 3234     | 3413    | 3232     |
|                   | 3369                | 3355    | 3330     | 3423    | 3301     |
|                   | 3436                | 3450    | 3444     | 3747    | 3365     |
|                   | 3583                | 3506    | 3743     |         | 3456     |
| C=O               | 1670                | 1645    | 1647     | 1660    | 1676     |
|                   | 1737                | 1660    | 1670     | 1733    | 1735     |
|                   |                     | 1733    | 1741     |         |          |
| CH3 & C-H         | 1080                | 1072    | 1081     | 1029    | 1074     |
|                   | 1157                | 1157    | 1157     | 1159    | 1155     |
|                   | 1245                | 1251    | 1249     | 1247    | 1244     |
|                   | 1373                | 1379    |          | 1375    | 1373     |
| Ti-O & Ti-O-Ti    | 435                 | 460     | 443      | 422     | 459      |
|                   | 486                 | 540     | 532      | 576     | 559      |
|                   | 649                 | 653     | 617      | 649     | 651      |
|                   | 734                 | 775     | 665      | 796     | 732      |
| CH2 & C–H         | 842                 | 873     | 838      | 840     | 842      |
|                   | 898                 | 929     | 898      | 896     |          |
|                   | 946                 |         |          |         | 946      |

Figures (3) shows the FTIR spectra for polymer blend and nanocomposites. The peaks (3436 ~ 3460) for (T4, T6, P4 & P6) became narrower and had high intensity.

![Figure (3)](image_url)
The low intensity of blend peaks (1245, 1670 & 3436) as shown in the table (3.4) may be due to that the incorporated actively interact with (PVP-co-VAc) molecules, and then disturb the interactions among (PVP-co-VAc) molecules. The introduction of nanoparticle makes the intensity of the band dramatically enhanced, which may be related to an overlapping effect, from the introduction of a large number of Nano bonds [13].

3.3 Tensile strength

From Figure (4-a) and Table (4), the result shows that the nanocomposites with type (I) of TiO$_2$ have the higher tensile strength value (64 MPa) for T2 and the higher elongation value (3.8) was for T5. While the nanocomposites reinforced with TiO$_2$ (II) shows that the tensile strength increase with increasing the weight ratio of TiO$_2$ except for sample P5 with (7.5 wt.%) TiO$_2$ as seen in Figure (4-b) and Table (4). The decrease in tensile properties can be related to the poor distribution or agglomeration of nanoparticles.

![Stress-strain curves for blend and nanocomposite films.](image)

**Figure 4.** Stress-strain curves for blend and nanocomposite films. (a) (CP) and (T1~T6) films, (b) (CP) and (P1~P6) films.

The various amount of TiO$_2$ (1, 2, 3.5, 5, 7.5 and 10 wt. %) was conventionally added to [CH/(PVP-co-VAc)] blend. From Table (4), it was found that the addition nanocomposite could
promote the physical properties and mechanical properties of the films because nanoparticles have significant surface and size effects. The higher nanoparticle content maybe lead to poor allocation of the nanoparticle across the matrix which caused the stress in the continuous phase to increase and promote poor tensile strength. The imperfect distribution of the nanoparticle can explain the reduction in tensile strength through the matrix [14,15].

Table 4. Tensile properties of the blend and the nanocomposite with TiO$_2$ (type I & II).

| Sample | Nano-type & percent wt.% | Tensile strength (MPa) | Elongation at Max. % |
|--------|--------------------------|-----------------------|----------------------|
| CP     | 0                        | 47.87                 | 2.689                |
| T1     | TiO$_2$ (I) 1            | 60.22                 | 0.7                  |
| T2     | TiO$_2$ (I) 2            | 64.95                 | 0.96                 |
| T3     | TiO$_2$ (I) 3.5          | 38.67                 | 1.920                |
| T4     | TiO$_2$ (I) 5            | 39.33                 | 1.891                |
| T5     | TiO$_2$ (I) 7.5          | 40                    | 3.8                  |
| T6     | TiO$_2$ (I) 10           | 40.1                  | 1.45                 |
| P1     | TiO$_2$ (II) 1           | 19.9                  | 0.12                 |
| P2     | TiO$_2$ (II) 2           | 24.87                 | 0.23                 |
| P3     | TiO$_2$ (II) 3.5         | 41.39                 | 2.680                |
| P4     | TiO$_2$ (II) 5           | 49.65                 | 2.489                |
| P5     | TiO$_2$ (II) 7.5         | 20.4                  | 0.46                 |
| P6     | TiO$_2$ (II) 10          | 70                    | 4.1                  |

The mechanical properties of the blend and nanocomposites are a result of the polymer conformation and the attraction energies between the [(PVP-co-VAc)/CH] chains [16,17].

3.4 Thermal conductivity
The thermal conductivity of blend (CP) and TiO$_2$ nanocomposite films result showed that the highest values of thermal conductivity were accomplished for the polymer blend (CP), (CH/[PVP-co-VAc]), while it decrees with increasing nanoparticle incorporation, as shown in Figure (5) & Table (5). Small particle size has a large surface area that means more considerable thermal interface resistance.
Table 5. The thermal conductivity of the blend and nanocomposites films.

| Sample type | Nano wt.% | Type of nano TiO₂ | Thermal conductivity (W/m.k) |
|-------------|-----------|-------------------|-----------------------------|
| CP          | -         | -                 | 0.106761                    |
| T1          | 1         | TiO₂(I)           | 0.099552                    |
| T2          | 2         | TiO₂(I)           | 0.098553                    |
| T3          | 3.5       | TiO₂(I)           | 0.097307                    |
| T4          | 5         | TiO₂(I)           | 0.093597                    |
| T5          | 7.5       | TiO₂(I)           | 0.093316                    |
| T6          | 10        | TiO₂(I)           | 0.090003                    |
| P1          | 1         | TiO₂(II)          | 0.088163                    |
| P2          | 2         | TiO₂(II)          | 0.073552                    |
| P3          | 3.5       | TiO₂(II)          | 0.066779                    |
| P4          | 5         | TiO₂(II)          | 0.069047                    |
| P5          | 7.5       | TiO₂(II)          | 0.061471                    |
| P6          | 10        | TiO₂(II)          | 0.066767                    |

Figure 5. Thermal conductivity of (CP) blend and nanocomposite films.

3.5 Water absorption

Swelling behavior of blend [CH/(PVP-co-VAc)] film and [CH/(PVP-co-VAc)/TiO₂], [CH/(PVP-co-VAc)/CaCO₃] nanocomposite films were done by using rectangular samples with (10×10 mm). The result shows that the water uptake for the blend is higher than the other nanocomposite films, and the weight gain decrease with the increase of the nanoparticle as shown in Figure (6). The water uptake occurred due to the formation of micro-cracks and voids in the surface of the samples during the longer degradation stages. That may be expounded as the voids and flaws existing on the surface and inside the samples have been attacked and filled with the solution. This process occurred first, leading to swelling, the following step separates polymers chains apart, and the swollen polymer generates sufficient pressure to destroy the intermolecular chains, leading to polymer degradation. It is worth mentioning that the interfaces are prone to chemical attack, and this can be true for the blends, and after attacking the interfaces, liquids will diffuse into the material [18,19].
Figure 6. Effect of TiO$_2$ content on swelling behavior of blend (CP) at various interval time; (0.5, 1, 1.5, 2, 2.5, & 3 h), at RT for (a) (CP) and (T1-T6) and (b) (CP) and (P1-P6).

The water absorption of the blend film was the highest among the other films because chitosan has increased the hydrophilicity due to its hydroxyl groups (OH) and amino groups (NH$_2$) while that of (PVP-co-VAc) depends upon only hydroxyl groups (OH). Therefore, hydroxyl group can form stronger hydrogen bonds with water (H$_2$O) than an amino group [20], while the water gain of the nanocomposites is lower than the (CH/ PVP-co-VAc) blend because it contains TiO$_2$ the nanoparticles decreases and spread throughout the plastic and be able to block oxygen, carbon dioxide, and moisture [21].

4. Conclusions

Incorporation of the TiO$_2$ nanoparticle to the blend [CH/[PVP-co-VAc]] via solution casting method produced the TiO$_2$ nanocomposite films. The immobilized TiO$_2$ exhibited an excellent distribution in chitosan film when adding a small amount of TiO$_2$. The results show that the tensile strength of these nanocomposites was enhanced compared to the blend [CH/[PVP-co-
VAc)] film. The addition of nanoparticle to the blend reduced its absorption ability to the water as well as its thermal conductivity. The TiO₂ nanocomposites will be promising sources for photocatalyst materials for various organic compounds in the environment.

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