Synthesis and Characterization of the Composite Material PVA/Chitosan/5% Sorbitol with Different Ratio of Chitosan

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Abstract-- Composites of Poly (vinyl alcohol) (PVA)/Chitosan (CS) have been synthesized and characterized successfully. Mechanical and degradation properties of composites also have been modified. PVA/CS composites prepared with different concentration ratio of PVA/CS (90%PVA/10%chitosan, 80%PVA/20%chitosan, 70%PVA/30%chitosan, 60%PVA/40%chitosan and 50%PVA/50%chitosan). FTIR shows the changed in intensity and bonding as well as shifting in peaks with increasing of CS, and sorbitol. SEM micrographs of composites surface showed that CS partially miscible with high ratio of PVA. Mechanical properties were characterized and the result indicates that tensile strength and modulus of elasticity increased with increasing CS ratio which associated with decreasing in elongation and flexibility of films. By adding sorbitol, the elongation at break has been improved. Weathering of composites showed high degradation rate with higher CS concentration. Degradation of composites has been affected by the addition of sorbitol. A numerical study was conducted for the PVA/CS, the study gives a closed results compared with the experimental values.

Index Term-- PVA/Chitosan, Composites, Various Ratios, sorbitol, FEM analysis

1. INTRODUCTION
The concept of using long lasting polymers for short lived applications (e.g. packaging, catering, surgery, hygiene, etc.) is becoming increasingly unacceptable; however, this is not justified when increased concern exists about the preservation of ecological systems. Most of today’s synthetic polymers are produced from petrochemicals and are not biodegradable. These persistent polymers are a significant source of environmental pollution, harming wildlife when they are dispersed in the nature. Approximately 40 million tons of plastic packaging is used annually worldwide the majority of which are used once and discarded later [1]. Developing of biodegradable plastic materials is required by using natural sources such as starch, cellulose, chitosan. Chitosan is obtained from the deacetylation of chitin which is found in marine environments. Chitosan is insoluble in water, dissolved in acidic solutions before being incorporated into biodegradable polymer films [2, 3]. Chitosan has been used in very wide range of applications such as prevention of water pollution by chelating heavy metals, membrane separation in medicine and biotechnology, and in food packaging material [4, 5 and 6] PVA has found also in many applications in pharmaceuticals, cosmetics and in the paper and food industries, either alone or in blends with other polymers such as poly (3-hydroxy butyrate) [7]. Poly(vinyl) alcohol/chitosan blends have attracted more attention as a biodegradable polymer blends due to their excellent biocompatibility and suitable physical properties, which can be used in environmentally friendly materials such as packaging, membrane filtration, dye adsorption and biomedical materials for controlled release, improved comfort, reduced irritation, and tissue engineering [8,9 and 10] PVA/Chitosan is not fully miscible at molecular level. The miscibility between chitosan and PVA in the blend has been shown to depend on the preparation processing and the relative content of CS and PVA components [12, 13]. Poor miscibility between PVA and chitosan due to weak interaction between PVA and chitosan this problem could be addressed to some extent through modifying the basic interactions between CS and PVA using hydrogen bond forming plasticizer such as sorbitol. It is well known that the chemical nature of side chains of vinyl polymers acts as the main factor in their miscibility behaviors. PVA and CS have one and four hydroxyl groups in each unit, respectively. Strong interactions between them are thereby achievable by breaking their tight intramolecular structure. This will be helpful to improve their miscibility and some other performances. From this point of view, sorbitol employed as a possible candidate to modify the basic interaction between PVA and CS [14]. Few researchers have been studied the effects ratios of chitosan on the mechanical properties and biodegradable [1, 12, 15, 16, 17]. Therefore, in this study, poly (vinyl alcohol) has been selected to blend with chitosan to study in details the effects of chitosan and sorbitol ratios.
on the mechanical properties and biodegradable characterization of polymer. Several study were conducted to analyses the numerical behavior of discontinues composite materials [18, 19, 20 and 21]. In this work the chitosan particles is considered asperical, then by consideration of symmetry the RVE of composite is ¼ the volume of cube with sphere in the center of the cube. We have developed the numerical study and conducted an experimental-Numerical comparative analysis.

2. EXPERIMENTAL

2.1. Materials

In the present study, the starting materials chosen were Poly (vinyl alcohol), PVA powder (hydrolysis MW=89,000-98,000, Tm = 126 °C and density 1.4406 g/cm³) was purchased from Sigma –Aldrich 99+ product of USA. Chitosan is obtained from the deacetylation of chitin and can be extracted from shellfish such as shrimp, lobster and crabs. Generally Chitosan exists in a form of white, yellowish powder (density= 1.54483 g/cm³) was purchased from Mega Makmur (M) Sdn, Bhd. Acetic acid R-COOH (purity = 99.98, density = 1.05 g/cm³ with MW 60 g mol-1) was purchased from merck-Germany (catalog no. 10063). Sorbitol is a sugar alcohol that is also known as glucitol was purchased from Sigma –Aldrich, D- product of USA.

2.2. Sample preparation

PVA powders were dissolved in distilled water to maintain a 3% solution concentration and stirred in magnetic stirrer using hot plate stirrer with speed of 500 rpm for 40 min at 95 °C. After the solution was cooled down to room temperature then chitosan powder was dispersed in 100 ml of distilled water and stirred using magnetic stirrer for 30 min. 1 ml acetic acid was added into chitosan aqueous solution and mixed with 1500 rpm stirring speed for 24 h at room temperature. After 24 hours PVA was added to chitosan solution (with different concentration ratio of PVA and chitosan) then PVA/chitosan solution was stirred for 3–5 h with 900 rpm stirring speed at room temperature. PVA/chitosan concentrations ratio weights were 90/10, 80/20, 70/20, 60/40 and 50/50 and PVA/chitosan/sorbitol concentrations ratio weights were 90/10, 80/20, 70/30, 60/40, 50/50% with 5% sorbitol (plasticizer to enhance miscibility and mechanical properties) and the solution stirred for 20-30 minutes. Finally, mixed solutions were poured into a glass-dish and the distilled water was allowed to evaporate for 48 hours to produce the cast film as well as all PVA/CS and PVA/CS/ sorbitol composites have been vacuumed before any test took place. Then, when evaporation process is completed, PVA/chitosan composites were analyzed for bonding by FTIR as well as underwent mechanical testing. The composites were assessed using tensile testing to determine the tensile stress, modulus of elasticity and elongation at break for both cases. Morphology of composites analyzed by SEM. Water absorption for all composites with different concentrations has been performed where the samples were immersed into water and the degradation behavior was evaluated with respect to water absorption properties. Weathering for all composites has been investigated by exposing sample to atmosphere for one month.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 Fourier Transform Infra-Red (FTIR) Analysis

FTIR has been used as useful tool in determining specific functional groups or chemical bonds that exist in a material, particular deformation of the molecules, the movement of a group of atoms or the bending or stretching of a particular bond. For chitosan filled PVA composites, if specific interactions took place between the two polymers, the most obvious and significant difference would be the appearance of a new peaks or shift of existing peaks. The figure 1 shows the FTIR spectra of PVA/chitosan with difference concentrations where the peaks at 3420 cm⁻¹ concerned with –OH and –NH stretching vibrations broded and shifted obviously to a lower number with addition of PVA suggesting the formation of much hydrogen bond between PVA and chitosan while the peak at 3350 indicating most of the crosslink age were formed between the amino groups of chitosan but not hydroxyl groups of PVA. The sharp peaks at 3269 cm⁻¹ refer to the combination of –OH and –NH formation group where the overlapping of hydroxyls (–OH chitosan, and PVA) and amino (–NH, chitosan) and the peaks at 2990cm⁻¹ related to alkyl group. In addition another strong peak at 292 cm⁻¹ refer to CH₂ stretching vibration (PVA) another peaks appear at 1700-1725cm⁻¹ characteristic of the carboxylic acide due to presence of acitic acid and the peaks at 1653-1550 which corresponding to the formation of amine bond (C= N) which related to chitosan. Peaks at 1560-1548cm⁻¹ which are symmetric deformation of NH3+ resulting from ionization of primary amine groups in the acidic medium and the peak at 1408cm⁻¹ refer to carboxylic acid in polymer also the strong peaks at 1300-1210cm⁻¹ related to C-H vibration. The peaks 1071-835 cm⁻¹ are related to characteristic peaks of crystallization of chitosan (see figure 1).
From the figure 2 the peaks were mostly same to the films of PVA/chitosan where there no phase separation promoted because of the tendency of PVA to develop hydrogen bond with water and with plasticizer (sorbitol) which has hydroxyl groups. Furthermore, it is important to note that the presence of self-associated molecules such as water, sugar and PVA improves the compatibility of the PVA/chitosan blend. The peaks 3253, 2933, 1076, 1023 and 876 cm$^{-1}$ are shifted and intensity changes of the band have been related to the addition of the plasticizer in the PVA/chitosan composites.

3.2 SEM observations
PVA/chitosan is not compatible and immiscible with high PVA ratio which increasing the agglomerated chitosan in the film as shown in Figures 3 (A, B). The compatibility and immiscible have been increased with increasing chitosan
ratio with less agglomeration in composite as shown in Figures 4 (A, B, C, D and E).
Sorbitol employed as a possible candidate to modify the basic interaction between PVA and CS which lead to increasing miscibility, compatibility, and flexibility of the films. Figures 4(A to E) shows the SEM micrographs for the surface of PVA/chitosan blended with 5% sorbitol. miscibility, and compatibility with less agglomeration have been noticed with high ratio of chitosan as shown in Figure 4 D and E also the thickness of films with sorbitol were 0.25-0.33 mm whereas without sorbitol were 0.18-0.28 mm. By adding sorbitol the films were less sticky to the glass dishes.

Fig. 3. SEM micrographs for different PVA/chitosan consecration composites
3.3 Mechanical properties before and after withering

In this study the tensile test was carried out to evaluate the effect of chitosan and sorbitol as filler in PVA. The thickness of the film was mostly limited to less than 0.5 mm. The tensile strength, modulus of elasticity, and elongation of PVA/different Chitosan ratios and PVA/different Chitosan
ratios/5% sorbitol composites are presented in Figure 5 tensile strength, and modulus of elasticity clearly increased with increasing of brittle chitosan (before and after added Sorbitol) due to tensile strength for pure chitosan film (31.72 MPa) higher than pure PVA (2.703 MPa) and increasing chitosan ratio lead to more compatibility and miscibility with less agglomeration which also increase the tensile strength, and modulus of elasticity. By comparing the modulus of elasticity between pure PVA film and the 50% PVA 50% CS composite clearly noticed that the increasing about 31times. Elongation at break decreased with increasing of brittle chitosan (before and after added Sorbitol) due to its high crystalline and high glass transition temperature. Plasticizer (Sorbitol) was used to improve the ductility and biodegradability of the chitosan filled PVA film, and study the mechanical properties of plasticized PVA/chitosan blends.

Sorbitol as plasticizer but the elongation at break increased more than 21 times in (90% PVA +10% CS) composite. The sorbitol decrease the rigidity of the chitosan network and increasing the ability of movement of polymer chain due to the existing of hydroxyl group also the phase separation is not promoted because of the tendency of PVA to develop hydrogen bonds with water and plasticizers (sorbitol) which have hydroxyl groups. Meanwhile, chitosan films plasticized with sorbitol were brittle and cracking. Finally, sorbitol enables enough polymer chains to take place to allow them to align and form crystallites. The purpose of weathering is to know the influence of the natural on mechanical properties and degradation. The test was according to ASTM 570-98 and the period of the test was for one month and the temperature was in rang of 33-35 °C with rainy weather for the most of the period, 19 rainy days, where after the one month the sample was tested and the increasing of mechanical properties were founded with 90%PVA/10%chitosan and 80%PVA/20%chitosan due to crosslinking under the weathering condition as shown in figure 6.

From Figure 6 by increasing chitosan the elongation was decrease rapidly that due to the degradation and brittleness behavior of chitosan which influenced by the changing in the weathering while the tensile strength and modulus were decreased at steady rang.
Fig. 5. (A) Tensile Strength (B) Modulus of Elasticity (C) Elongation at break for PVA/ with different ratio of Chitosan composites after and before adding 5% sorbitol.
3.4 Water absorption and Degradability

Hydrophilicity and hydrophobicity are important characteristic of biomaterials where the water absorption is one of the parameters which used to determine the hydrophilicity of the materials. Water absorption of the composites is important characteristic that determine the application of this material where water absorption could lead to a decrease in some of the properties and should be considered when selecting the application of the PVA/chitosan composites. The equilibrated water content of the chitosan filled PVA films is shown in Figure 7. The water swelling was performed using distilled water with ph. 7.4 at 33 °C. The kinetics of water uptake displayed the typical increase with time until the equilibrium was reached. The swelling properties increased with time due to water absorption and the weight gain for each composite was measured at intervals time of 1 minute, 2, 5 minutes, 10 minutes, 15 minutes, 30 minutes, 1 hour, 2 hours, 4 hours 6 hours, 8 hours 10 hours 16 hours, 20 hours and 24 hours respectively. Interestingly, the increasing of chitosan in composites to have less stability and accelerate degradation where chitosan film is sensitive to water like many synthetic oxygen barrier [22]. In addition most protein film including chitosan films provide good gas barrier properties but have poor water barrier characteristics compare with synthetic films [23]. Chitosan is hydrophilic polymers which absorb a considerable amount of water at ambient temperature where the raw chitosan film is not soluble in water but it is damaged in structure to further test. The degradation of chitosan in distilled water was reported to occur via the residual OH and NH₂ groups which found in pure chitosan film where these groups interacted with water molecules through hydrogen bonding [24]. PVA will improve the capability of chitosan film to absorb and hold water because PVA is the synthetic component of the blends, consists of somewhat crystalline junction zones and amorphous regions, and is a highly hydrophilic polymer, whose physical properties are strongly influenced by absorbed water where it has been noticed that the water content increase with increasing PVA ratio and the moisture content increased with increase in PVA concentration as shown in Figure 7. Since the samples were dense composites; the water uptake will affect the volume of the composites significantly where within one hour of immersion in distilled water, composite with 50%chitosan showed the lowest swelling percentage with 17.3%. Consequently, the increasing for (90% PVA / 10% chitosan) is 125.5%, for (80% PVA / 20% chitosan) is 97.8%, 91% for (70% PVA / 30% chitosan), 42.8% for (60% PVA / 40% chitosan) and finally 17.3% for (50% PVA / 50% chitosan) of weight increased. The first stage of water absorption for PVA/chitosan exhibits rapid weight gain (water absorption) which is then followed by a relatively static stage in which water permeate into crystalline zone.
From the results it's clearly noticed that the water uptake ratio is increase with increased of PVA content in the composites and the first composite which reach to steady state and stability is the one with lowest PVA ratio. The composites of PVA/chitosan with 5% sorbitol as in Figure 8 reached to equilibrium state more rapidly than PVA/chitosan composites because of sorbitol, D-glucitol (C₆H₁₄O₆), white powder is very soluble in water.
The films with higher chitosan concentration show more compatibility and rapid degradation than others films which indicates chitosan films support the degradation process for the PVA films and take less time to fully degraded. The composites of PVA/chitosan containing sorbitol degraded faster than the sample contain no sorbitol where the film (50% PVA/50% chitosan with 5% sorbitol) degraded and lost structure within nine days and the film (60% PVA/40% chitosan with 5% sorbitol) degraded and have been lost its structure within eleven days due to the high content of chitosan in the film, and sorbitol which is very sensitive to the water and moisture while the composite with 70% PVA and 30% chitosan has been degraded within 19 days because of less chitosan content as well the composites with 80% PVA/20% chitosan and 90% PVA/10% chitosan have been degraded within 30 days. The climate over here is of equatorial type in which the temperature is quite uniform throughout the year with temperature ranging from 21°C to 32°C. The humidity is consistent in the region of about 75% to 80%, and that influence and accelerated the degradation process and shown in Figure 9.

Fig. 9. Degradation of different PVA/chitosan concentration composites film with 5% sorbitol E) 50% PVA and 50% chitosan.
4. NUMERICAL STUDY

The numerical study of elastic behavior of the composite material is based on the periodic homogenization method using the computer code Abaqus. We focused on PVA/chitosan blended with 50% CS, and the composite structure can be approached to spherical filler drowned homogenously in the matrix as a square mesh. The representative Volume Elementary (RVE) chosen is a cube of matrix and one sphere of filler. By considering the symmetry of RVE, the problem can be solved as just the eighth of the cell. Consequently, RVE studied is a cube (a=0.5) and 1/8 of a sphere (see figure 10).

![Fig. 10. The numerical model of the RVE of PVA/CS with 50% of CS](image)

In order to calculate the composite’s properties it is necessary to apply the rule-of-mixtures, the volume fraction or weight fraction of each constituent must first be determined.

Volume fraction of the chitosan component \( V_f \) is defined as:

\[
V_f = \frac{v_f}{v_c}
\]  

(1)

where \( v_f \) is the volume of the chitosan fiber and \( v_c \) is the volume of the composite.

Similarly the weight fractions \( W_f \) and \( W_m \) of the fiber and matrix respectively can be defined as

\[
W_f = \frac{m_f}{m_c}
\]  

(2)

To convert between volume fraction and weight fraction consider the definition of weight fraction and express the weights in terms of volumes and densities.

Then :

\[
\frac{v_f}{m_f} = \frac{\rho_c}{\rho_f}
\]  

(6)

With:

\[
\rho_c = \frac{1}{\frac{v_f}{\rho_f} + \frac{v_m}{\rho_m}}
\]  

(7)

\[
\langle \sigma; \varepsilon \rangle = \langle \sigma \rangle = \sum: E
\]  

(8)

The macroscopic stress \( \langle \sigma; \varepsilon \rangle \) is a linear function of the macroscopic strain:

\[
(E = < \sum >)
\]  

(9)

Assuming that the elastic behavior of composite material is orthotropic, we resolved the relationship presented in equation (8) [18, 19].

The Hooke criteria can write as follow:
The calculation of the $C_{ijkl}^{\text{hom}}$ coefficients takes place while calculating the stress field that corresponds to an imposed macroscopic displacement (see figure 11). Supposing that the RVE of the composite with orthotropic characteristic, the macroscopic elasticity relation is expressed as follow:

$$
\Sigma = C^{\text{hom}} E
$$  \hspace{1cm} \text{(10)}

Where $C^{\text{hom}}$ represents the macroscopic stiffness matrix obtained by the homogenization method.

Then:

$$
\begin{bmatrix}
\Sigma_{11} \\
\Sigma_{22} \\
\Sigma_{33} \\
\Sigma_{23} \\
\Sigma_{13} \\
\Sigma_{12}
\end{bmatrix} =
\begin{bmatrix}
C_{1111}^{\text{hom}} & C_{1211}^{\text{hom}} & C_{1311}^{\text{hom}} & 0 & 0 & 0 \\
C_{1122}^{\text{hom}} & C_{1222}^{\text{hom}} & C_{1322}^{\text{hom}} & 0 & 0 & 0 \\
C_{1133}^{\text{hom}} & C_{1233}^{\text{hom}} & C_{1333}^{\text{hom}} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{2222}^{\text{hom}} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{3333}^{\text{hom}} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{1212}^{\text{hom}}
\end{bmatrix}
\begin{bmatrix}
E_{11} \\
E_{22} \\
E_{33} \\
E_{23} \\
E_{13} \\
E_{12}
\end{bmatrix}
$$  \hspace{1cm} \text{(11)}

Fig. 11. The imposing macroscopic deformation and boundary conditions: simple traction displacement (a) and simple shear displacement (b)

For $i = j = k = l$; $i, j, k, l \in \{1,2,3\}$, the $C_{ijkl}^{\text{hom}}$ coefficients it determined by imposing to the basic cell a simple traction displacement on the main directions correspond with the symmetry’s axes of the cell; that’s means:

$$
E_i = E_{11} e_i \otimes e_i + E_{12} e_i \otimes e_2 + E_{13} e_i \otimes e_3
$$  \hspace{1cm} \text{(12)}

For $i = k$ and $j = l$; $i, k \in \{1,2\}$ and $j, l \in \{2,3\}$, the coefficients $C_{ijkl}^{\text{hom}}$ it determined by imposing to the basic cell a macroscopic displacement of type simple shear which can be expressed as follow:

$$
E_i = E_{ij} / 2 (e_i \otimes e_j + e_j \otimes e_i)
$$  \hspace{1cm} \text{(13)}

A simple of the simulation obtained on the RVE is presented in the figure 12.
The numerical results obtained are given in the stiffness matrix in equation (14). (All terms of the matrix are expressed in MPa). This result shows that the composite material is isotropic.

\[
\mathbf{C} = \begin{bmatrix}
2333.18 & 1423.85 & 1423.86 & 0 & 0 & 0 \\
1423.85 & 2333.18 & 1423.86 & 0 & 0 & 0 \\
1423.86 & 1423.86 & 2333.19 & 0 & 0 & 0 \\
0 & 0 & 0 & 454.43 & 0 & 0 \\
0 & 0 & 0 & 0 & 454.43 & 0 \\
0 & 0 & 0 & 0 & 0 & 454.44 \\
\end{bmatrix}
\]

(14)

A comparison between the Young modules, Shear Modules and Poisson’s ratios calculated numerically and those measured experimentally from the identification of the elastic behavior of composite PVA/Chitosan is presented in Table 1.

The numerical study gives a closed results compared with the experimental values. The variation between the numerical Young modulus E is less than the experiment of 11.8% and the value of numerical G is less than the experiment of 12.4 %. This deference it is may be due to the effect of banding between the CS and the PVA. Then to reduce the error between numerical and experimental results it is recommended to develop a specific behavior model for the interface PVA/Chitosan.

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5. CONCLUSIONS
Composites of Poly (vinyl alcohol) (PVA)/Chitosan (CS) have been synthesized and characterized successfully. PVA/CS and PVA/CS/5% sorbitol composites have been prepared with different concentration ratio of PVA/CS. FTIR shows the changed in intensity and bonding as well as shifting in peaks with increasing of CS, and sorbitol. The compatibility and immiscible have been increased with increasing chitosan ratio with less agglomeration. Tensile strength and modulus of elasticity increased with increasing CS ratio which associated with decreasing in elongation and flexibility of films. Elongation at break has been improved.
by adding sorbitol. The composites have been showed high degradation rate with 5% sorbitol 50% PVA and 50% chitosan. 

The numerical study of the composite PVA/CS gives a closed results compared with the experimental values. The deference on values it may be due to the effect of banding between the CS and the PVA. Then to reduce the error between numerical and experimental results it is recommended to develop a specific behavior model for the interface PVA/Chitosan.

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