

Effect of nanoSiO₂ Additive of Some Mechanical and Water Absorption of Polyvinyl Alcohol/Chitosan Blends

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ABSTRACT

Polyvinyl alcohol/Chitosan blend (PVA/CC(50:50) and (PVA/CC/10wt% SiO₂) composite, were prepared by casting method on a glass plate. Poly (vinyl alcohol)-chitosan blend films were prepared with a thickness about 250 micron. The crystalline structure of PVA and fingerprint of semi-crystalline of chitosan was confirmed by X-ray diffraction. The tensile results show that the tensile strength and Young's modulus of these hybrid films were greatly improved compared to the neat PVA film which was 10.86 MPa, 82GPa respectively and for the sample containing 10 wt% silica was 20.6 MPa and 227GPa respectively where compared to PVA/CC which was 15.93 MPa and 131GPa respectively. Strong interfacial bonding between the silica and the PVA/CC, and homogenous distribution of the silica particles in PVA/CC are supportive of markedly improved mechanical strength. The solubility measurements showed that the hybrid has an enhanced water resistance, the solubility decreased with the addition of silica. Blending PVA and chitosan improved strength and young modules of the film and increased water uptake because hydrophobicity of two polymers blend films.

Key words: PVA, Chitosan, Nano SiO₂, XRD, FTIR, Tensile strength, Water Absorption

INTRODUCTION

There is growing interest in recent times to develop materials with film forming capacity and having antimicrobial properties which improve food safety and shelf-life. Antimicrobial packaging is one of the most promising active packaging systems, the use of such packaging is not meant to be a substitute for goods animation practices, but it should enhance the safety of food as an additional hurdle for the growth of pathogenic and/or spoilage microorganisms (Tripathi et al, 2009). Barrier film technologies protect food from deterioration by reducing or eliminating oxygen and water vapor permeation. Barrier films are becoming more widespread, in part because of increasing popularity of prepackaged food (EL-HEFIAN et al, 2010).

Poly(vinyl alcohol) (PVA) a biodegradable, synthetic polymer, innocuous, non-carcinogenic and have good biocompatible properties. Poly (vinyl alcohol) has excellent film forming properties. Because of its good film forming and highly hydrophilic water soluble with

outstanding chemical stability it was blended different synthetic and natural polymers, the use of this polymer is important in many applications such as controlled drug delivery systems, membrane preparation, recycling of polymers and packaging (Duncan, 2011). Chitosan also represents interesting properties such as excellent film forming capacity and gas and aroma barrier properties at dry conditions, which makes it a suitable material for designing food coatings and packaging structures. All the above-mentioned properties also make chitosan a very good candidate to design novel antimicrobial active packaging technologies to improve the quality and safety and to extend the shelf-life of perishable foods (Zheng et al, 2001).

A number of other nanomaterials can be added on their own, or in addition to nanoclays, to polymers to provide additional barrier or functional properties for food packaging purposes. These include metal and metal oxide nanoparticles, nanofibres and nanotubes. Silica nanoparticles can be inserted into certain polymer matrices (such as polypropylene or starch) to improve mechanical or barrier properties of composites and biodegradable films. The purpose of this work is to study the optical, physical, and tensile properties of PVA/Cs blend with addition of nano silica dioxide SiO₂ composite.

EXPERIMENTAL WORK

Materials

PVA was purchased from Aldrich Co. (with 99% hydrolyzed, Mw 16,000) chitosan (CC) (high M.W, > 75% deacetylated) is purchased from Sigma Chemical Company (St. Louis, USA). Acetic acid (glacial, 99-100%), distilled water is used for the preparation, nanoSiO₂ particle size (20 nm) from sigma-aldrich company

Preparation of PVA/Chitosan blend Films

50 ml of chitosan solution (1% wt./wt. in acetic acid) and 50 ml of PVA solution (1% wt./wt. in water) (1:1) are mixed in 250 ml beaker and stirred for 1 h at 60°C to obtain homogeneous solution. The solution is transferred immediately into polystyrene Petri dishes and dried at 60°C in an electric oven for 48h. The films were peeled off and measured thickness in micrometer found it is 250µm and kept under evacuated desiccators over fresh silica gel until use.

Preparation of PVA/CC /nanoSiO₂ Films

PVA/CC nanocomposites preparation in weight (10wt%) the nanoSiO₂ are weighted and manually mixed with PVA/CC blend were mixed by shearing mixer at 800 rpm for 15 minutes to have good distribution. Distribution of the PVA/CC/SiO₂ components on the surface of these composites was investigated by optical microscopy, was compared with that in the PVA/CC and appear good distribution Fig(2 a, b)



a :PVA/CC



b: -PVA/CC/SiO₂

Fig(1): Optical microscopy of blend and composites PVA

FTIR

Spectra were recorded in KBr discs on a Shimadzu FTIR model 8000 Testcan IR-spectrometer under dry air at room temperature within the wave number range of 4,000–500 cm⁻¹.

X-ray Diffraction

X-ray Diffraction was done using a Brüker D8 Advance instrument, at 40 KV, 40 mA using target Cu K α with secondary monochromator (Karlsruhe, Germany)

Tensile Properties

The samples were prepared as films and their tensile strength using (Instron Co., Norwood, MA, USA), with a 65N load cell). Was used to measure tensile strength, young's modulus .The tests were carried out according to ASTM D-638 standard. Two metallic grips were attached for gripping both ends of the test specimen of the film. The modulus of elasticity (Young's modulus) was determined according to the following equation

$$\text{Tensile strength (N/mm}^2\text{)} = \text{Force (F)} / \text{Area (A)} \dots\dots\dots 1$$

$$\text{Elongation (\%)} = \text{Increase in length}(\Delta L) / \text{Original length}(L_0) \times 100\% \dots\dots\dots 2$$

$$\text{Young modulus} = F L_0 / A \Delta L \dots\dots\dots 3$$

Where:

F: force exerted on an object under tension, L₀: original length, A :cross section area, ΔL : length of the object changes

Water Uptake

The water uptake of different samples was calculated using the following method:

$$\text{Water uptake (M\%)} = 100 \times (W_2 - W_1) / W_1 \dots\dots\dots 4$$

$$\text{Diffusion Coefficient (D)} = \pi (Kb / 4M\infty)^2 \dots\dots\dots 5$$

$$\text{Permeability (P)} = 1000(\Delta M) / NV \dots\dots\dots 6$$

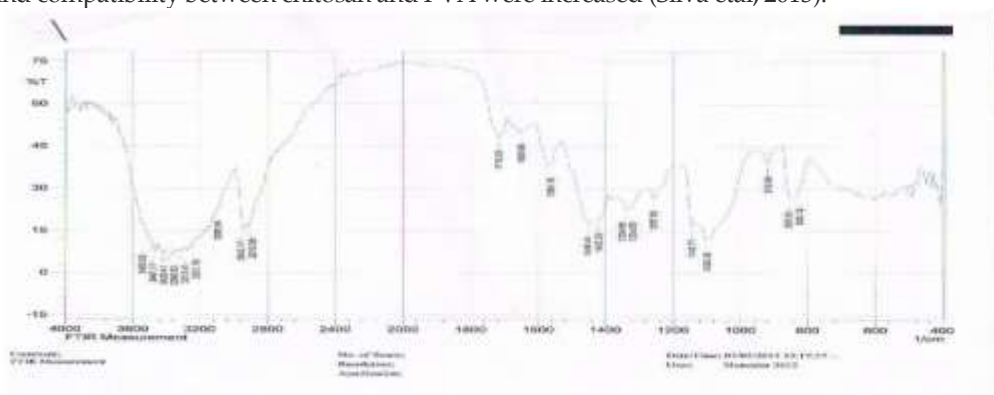
Where:

W₁: is the weight of completely dried sample ,and W₂: is the weight of swelled sample in solution at 25 C for 7 days , K: is the slope of curve between mass gain and immersion time , b: thickness of sample , M ∞ :saturation moisture mass , N number of day stored sample , V: volume of container cup.

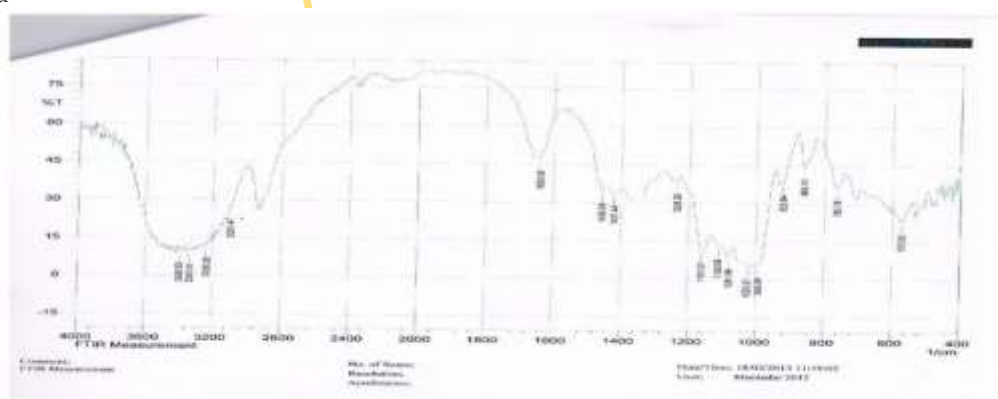
RESULTS AND DISCUSSION

FTIR

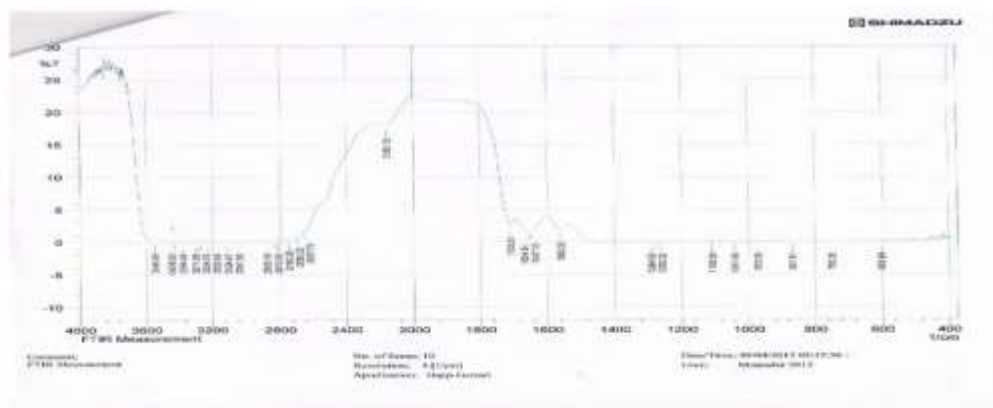
FTIR spectra of chitosan and PVA/CC film are shown in Fig(3). Stretching vibration spectra of the amide group of chitosan films appear at 1560 cm^{-1} . The change in the characteristic shape of the chitosan spectrum as well as shifting of peak to a lower frequency range due to hydrogen bonding between $-\text{OH}$ of PVA and $-\text{OH}$ or $-\text{NH}_2$ of chitosan in the blended films. This is due to the fact that when two or more polymers are mixed, changes in characteristic spectra peaks occur due to the reflection of the physical blends and chemical interactions. These observations indicate the existence of good miscibility between chitosan and PVA(50:50) and this is most likely due to the formation of intermolecular hydrogen bonds between the amino and hydroxyl groups in chitosan and the hydroxyl groups in PVA (Parvin et al, 2010). The results obtained in this study indicated that the nano- SiO_2 particles were dispersed evenly within the chitosan /PVA and an intermolecular hydrogen bond and a strong chemical bond $\text{C}-\text{O}-\text{Si}$ were formed in the nano- SiO_2 and chitosan /PVA. A hydrogen bond was formed in nano- SiO_2 and chitosan /polyvinyl alcohol (PVA), and intermolecular hydrogen bonding of the chitosan was decreased at the addition of nano- SiO_2 . Meanwhile, the chemical bond $\text{C}-\text{O}-\text{Si}$ was also formed in nano- SiO_2 /chitosan /PVA hybrid materials; therefore, the miscibility and compatibility between chitosan and PVA were increased (Silva et al, 2013).



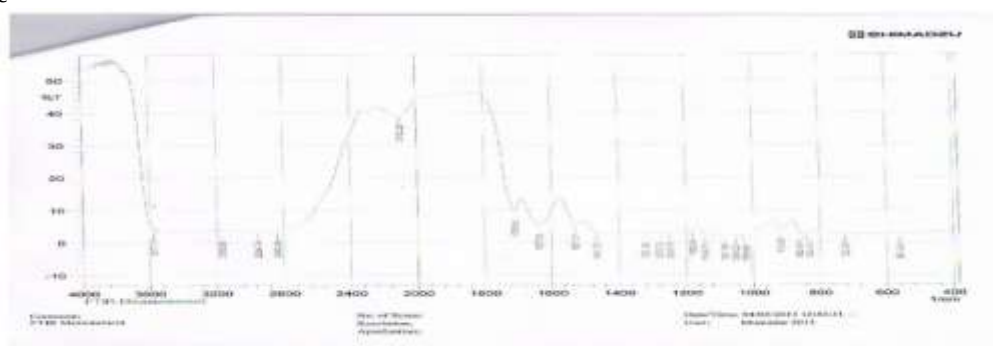
a



b



c



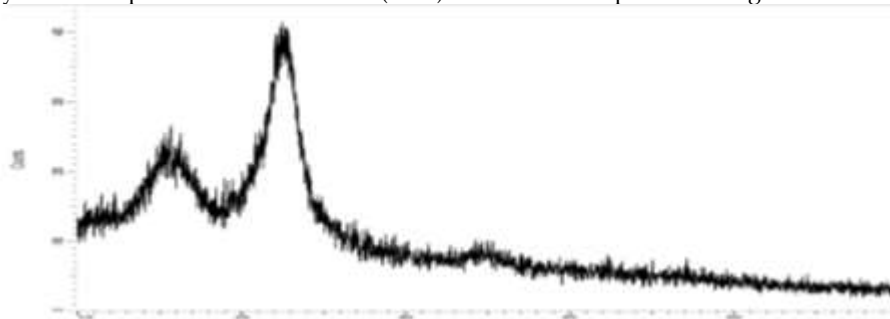
d

Fig(2):FTIR of a:PVA ,b:chitosan , c:PVA/CC, d:PVA/CC/SiO2

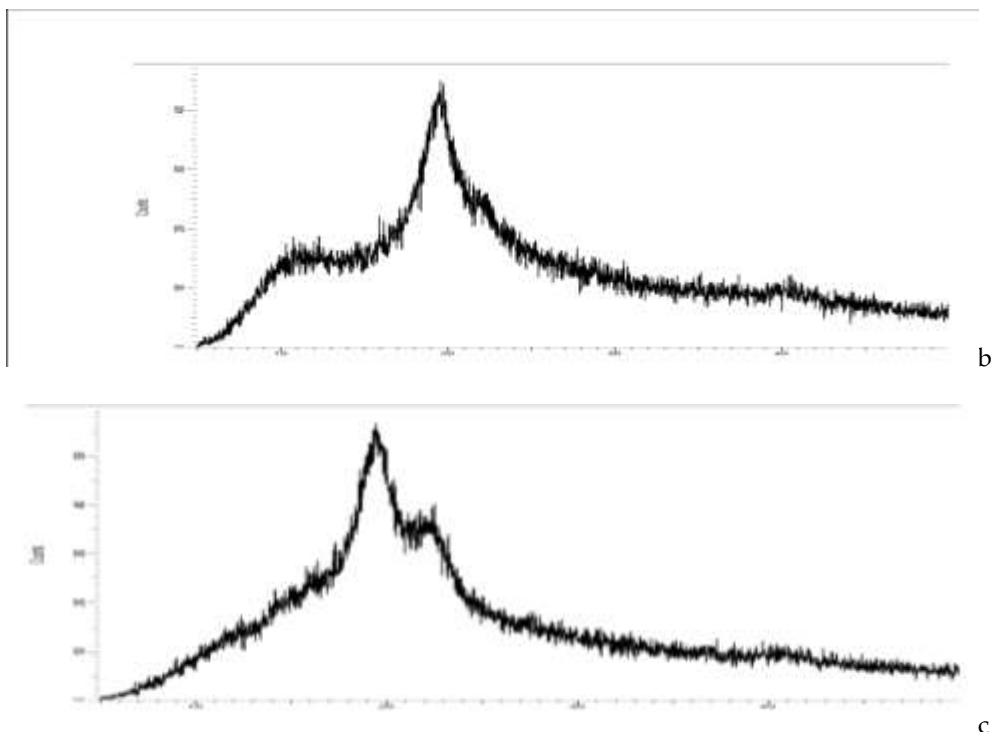
X-ray

X-ray diffraction is a proven tool to study crystal lattice arrangements and yields very useful information on degree of sample crystallinity. X-ray patterns of polyvinyl alcohol is located at $2\theta = 16^\circ$ and 23° and they are strong and intense indicating the high crystalline structure of PVA. The XRD pattern of chitosan exhibits broad diffraction peaks at $2\theta = 10^\circ$ and 20° which are typical fingerprints of semi-crystalline. Md. Monarul et.al have find that x-ray of chitosan exhibits broad diffraction peaks at $2\theta = 10^\circ$ and 21° which are typical fingerprints of semi-crystalline chitosan (Islam etal, 2008).

X-ray diffraction patterns of chitosan: PVA(50:50) show diffractive peak in the region from $2\theta = 20^\circ$.



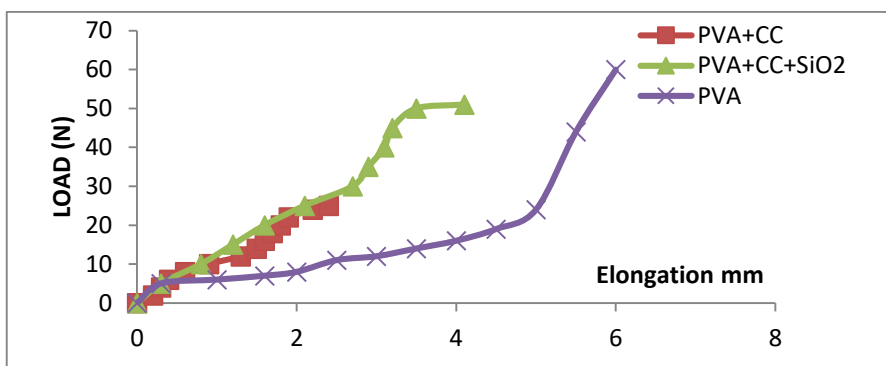
a



Fig(3) X-ray diffraction spectra of a: PVA b:chitosan c:PVA/CC blend

Tensile Properties

The tensile testing provides an indication of the strength and elasticity of the films, which can be reflected by strength and strain-at-break. The pure PVA film showed the tensile strength at 10.86 MPa. Blending PVA-CC improved tensile strength compared of PVA and become 15.93, . These results indicate that blend films have higher tensile strength than pure PVA films. S. Bahram et.al have also supported this results and find of blend PVA/CC that tensile strength is 19MPa(Bahrami etal, 2003). When add nano SiO₂ (10%) the tensile strength and Young modulus increased and become 20.6 MPa and 227GPa respectively that because nanoparticles have significant surface effects, size effects, that improve material properties.



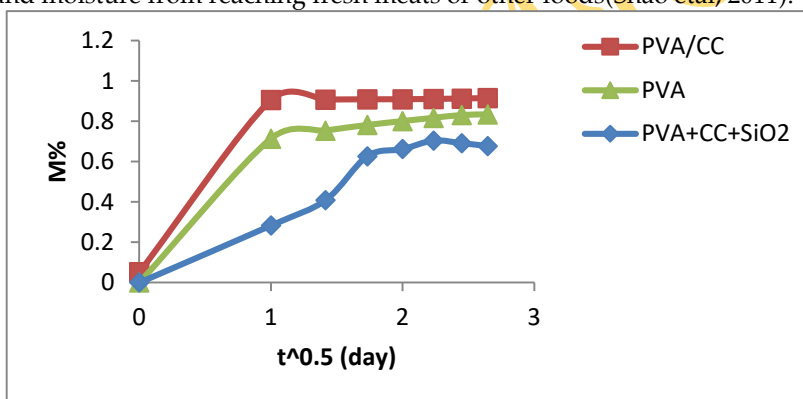
Fig(4) load and elongation curves of PVA, PVA/CC, PVA/CC/SiO₂

Table (1) Mechanical properties of blended and composites films

Sample	Tensile strength(MPa)	Young modulus (GPa)
PVA	10.86	82
PVA/CC 50:50	15.93	131
PVA/CC/SiO ₂ (10%)	20.6	227

Water Uptake and permeability

As shown in Table (2) water uptake of pure PVA decrease because nature of hydrophilic and depends upon only hydroxyl groups (OH) and blend of chitosan is increased the hydrophilicity because its hydroxyl groups(OH) and amino groups (NH₂) while that of PVA depends upon only hydroxyl groups (OH). Therefore hydroxyl group can form stronger hydrogen bonds with water (H₂O) than an amino group. This could be one reason why membranes with a higher content of chitosan (50–100 wt.%) in the polymer produced higher water permeation fluxes (Svang-Ariyaskul et al, 2008). The water uptake of the composites are lower than the PVA/CC blend because contain nano SiO₂ decreases nano particle are spread throughout the plastic and are able to block oxygen, carbon dioxide and moisture from reaching fresh meats or other foods(Shao et al, 2011).



Fig(5): Water Uptake of blend and composites films .

Table (2): Water Uptake and permeability of blended and composites films.

Sample	D(mm ² /day)	P(gm/day.ml)
PVA pure	2.77E-07	4.385714
PVA/CC 50:50	3.69E-07	5.785714
PVA/CC/SiO ₂ (10%)	1.54E-05	3.407143

CONCLUSION

In this study the blending of PVA /CC film prepare under 70C° and composites in presence of nano SiO₂, have been successfully prepared by the solution-casting technique. The FTIR XRD give the characteristic of pure PVA, Chitosan , PVA/CC, PVA/CC/SiO₂, tensile strength an Young modulus of composites increased compare in PVA pure and blend of chitosan.

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