Iraqi Journal of Physics, 2018 *Vol.16, No.39, PP. 11-22*
DOI: 10.20723/ijp.16.39.11-22

Study the effect of $CaCO_3$ nanoparticles on physical properties of biopolymer blend

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Abstract

Chitosan (CH) / Poly (1-vinylpyrrolidone-co-vinyl acetate) (PVP-co-VAc) blend (1:1) and nanocomposites reinforced with $CaCO_3$ nanoparticles were prepared by solution casting method. FTIR analysis**,** tensile strength, Elongation, Young modulus, Thermal conductivity, water absorption and Antibacterial properties were studied for blend and nanocomposites. The tensile results show that the tensile strength and Young's modulus of the nanocomposites were enhanced compared with polymer blend [CH/(PVP-co-VAc)] film. The mechanical properties of the polymer blend were improved by the addition of $CaCO_3$ with significant increases in Young's modulus (from 1787 MPa to ~7238 MPa) and tensile strength (from 47.87 MPa to 79.75 MPa). Strong interfacial bonding between the $CaCO_3$ nanoparticles and the [CH/(PVP-co-VAc)), homogenous distribution of the nanoparticles in the polymer blend, are assistance of noticeably raised mechanical durability. The thermal conductivity of the polymer blend and $CaCO_3$ nanocomposite films show that it decreased in the adding of nanoparticle $CaCO_3$. The solvability measurements display that the nanocomposite has promoted water resistance. The weight gain lowered with the increase of nano $CaCO_3$. Blending chitosan CH with (PVP-co-VAc) enhanced strength and young modules of the nanocomposites and increased the absorption of water because hydrophilic of the blended polymers films. The effect of two types of positive S.aurous and negative E. coli was studied. The results showed that the nanocomposites were effective for both types, where the activity value ranged from (12 ~ 21). The best results were found for S.aurous bacteria.

Key words
Natural polymer, nanocomposites, physical properties, antibacterial, calcium carbonate nanoparticles.

Article info.
Received: May. 2018
Accepted: Jun. 2018
Published: Dec. 2018

دراسة تأثير الجسيمات النانوية $CaCO_3$ على الخواص الفيزيائية لخليط احيائي بولمري

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الخلاصة

مزيج الشيتوسان(CH) و Poly (1-vinylpyrrolidone-co-vinyl acetate (CH/[PVP-co- VAc]) بنسب (1:1) ومركب النانوي المعزز بحجمين من جسيمات الـ $CaCO_3$ النانوية قد تم إعدادها بطريقة صب المحلول. تمت دراسة تحليل الـ FTIR، خواص قوة الشد، الاستطالة، معامل يونك، التوصيلية الحرارية، امتصاصية الماء و الفعالية البايولوجية للمزيج والمتراكب النانوي. أظهرت نتائج الشد أن قوة الشد ومعامل يونك لأغشية المركب النانوي تحسنت مقارنة بافلام مزيج البولمر [CH/(PVP-co-VAc)]. ان اضافة المادة النانوية $CaCO_3$ للمزيج البولمري [CH/(PVP-co-VAc)] ادى الى زيادة في قوة الشد (من 47.87 MPa إلى 79.75 MPa) ومعامل يونك (من 1787 MPa إلى ~ 7238 MPa). الترابط البيني القوي بين الجسيمات

النانوية $CaCO_3$ و (CH/ [PVP-co-VAc)]، التوزيع المتجانس للجسيمات النانوية في مزيج الـ (CH / [PVP-co-VAc]) هي الداعمة للخواص الميكانيكية المحسنة. اظهرت التوصيلية الحرارية لافلام المزيج (CH/[PVP-co-VAc]) والمتراكب النانوي (CH/ [PVP-co-VAc)] / $CaCO_3$) ان اضافة المادة النانوية $CaCO_3$ ادت الى انخفاض في قيم التوصيلية الحرارية. أظهرت قياسات الذوبان أن المركب النانوي لديه مقاومة لامتصاص الماء. انخفضت امتصاصية الماء بزيادة $CaCO_3$ نانو. مزيج الشيتوسان CH مع (PVP-co-VAc) حسن قوة الشد ومعامل يونك للافلام وكذلك من امتصاصية الافلام للماء بسبب كون المادتين محبة للماء اي لديها ميل للخلط، ذوبان، والترطيب بالماء. تم دراسة المركب النانوي كتطبيق بايولوجي، حيث تم دراسة الفعالية البالوجية لنوعين من البكتريا الموجبة S.aurous والسالبة E.coli، وقد اظهرت النتائج ان المركب النانوي فعال لكلا النوعين، حيث كانت قيمة الفعالية تتراوح (12-21). وبالنتيجة وجد ان أفضل النتائج كانت للبكتيريا S.aurous.

Introduction

Chitosan (CH) is a natural polymer derived by deacetylation of chitin, which is the second most numerous polysaccharide found in nature. Natural polysaccharide chitosan, a derivative of chitin, is of great benefit as an organic component in the composites sophisticated for water treatment because of the high amount of amino and hydroxyl groups, which is very significant for sorption processes [1]. Furthermore, chitosan owned such properties as good biocompatibility, high adhesion to the surface, a wide range of pH stability, and expressed chelating properties. It has been proved that chitosan is influential bioadsorbent towards some toxic ions, dyes, and organic contaminants. Several procedures have been developed and proposed by many researchers over the years for the preparation of chitosan from different crustacean shell wastes. Some of these formed the basis of chemical processes for the industrial production of chitosan. Few attempts have been made to compare functional properties of chitosan prepared from various processes with those of commercially available chitin and chitosan products [2]. Poly (1-vinylpyrrolidone-co-vinyl acetate) (PVP-co-VAs), is one of the most used non-ionic amphiphilic copolymers, is soluble in both hydrophilic liquids such as water and hydrophobic solvents and chemically stable. Biodegradable (PVP-co-VAs) film with good plasticity and elasticity can be formed in water as well as organic solvents [3]. Using this property, it has been applied to gold colloids and platinum nanocatalysts, but not tried for iron nanoparticles up to date [4, 5]. Nanocomposites are an attractive class of materials providing new performance. As a result of some of their remarkable properties at low filler loading (less than 10 wt %), they are being increasingly adopted by industry whilst displacing the use of conventional filler materials. Polymer nanocomposites present a radical alternative to conventionally- and macroscopically-filled polymers [6]. A variety of nanoscale fillers, including layered silicates and nanoparticles, are capable of enhancing mechanical and thermal properties of nanocomposites, including modulus, strength, impact performance, and heat resistance [7-9]. Among nanoparticles, $CaCO_3$ is one of the most common and inexpensive inorganic fillers that has been used in the nanocomposite preparation process. The blending 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. To enhance the mechanical properties with degradability of chitosan films, Poly (1-vinylpyrrolidone-co-vinyl acetate) was select to blend with chitosan [10-12]. In this work, we report the effect of $CaCO_3$ nanoparticle on the tensile properties of polymer blend [CH/(PVP-co-VAc)] in addition to some of the physical properties.

Experimental procedure

(CH) is a natural carbohydrate biopolymer obtained from Sigma-Aldrich, had a medium molecular weight of 161.16 g/mol. ($CaCO_3$) Nanoparticles are typically 30 (nm) with the specific surface area (SSA) in the 30 - 60 m^2/g range. [PVP-co-VAc] with an MW of $\sim 5.0 \times 10^4$ $g.mol^{-1}$ were obtained from Sigma-Aldrich.

1. Film preparation

The blend of (CH) and (PVP-co-VAc) with the fixed weight ratio (1:1) was 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, and then mixed together with continuous stirring for about 1 h. Finally, cast in a petri dish of 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 ^oC in an electric oven at for 6 h. The films were peeled off and measured the thickness by a micrometer. For the nanocomposite preparation, after preparing the blend, then we add the $CaCO_3$ nanoparticles slowly to the solution and keep it in continuous stirring for 30 min. The weight ratio of $CaCO_3$ nanoparticles used in preparing nanocomposites was listed in Table 1.

Table 1: Illiterate the name and the percentage of the polymer [CH/ (PVP-co-VAc)] and $CaCO_3$ nanoparticles.

Sample name	[CH/(PVP-co-VAc)]	$CaCO_3$ %wt.
CP	1:1	0
A1	1:1	2
A2	1:1	3.5
A3	1:1	5
A4	1:1	7.5
A5	1:1	10

2. Characterizations of films

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.

Tensile strength

The tensile strength of [CH/(PVP-co-VAc)] blend and $CaCO_3$ nanocomposite specimens were characterized for their properties in the longitudinal direction in accordance with ASTM D882-02. The films were cut into slices with a dimension of 10 mm x 80 mm and with the 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 $mm.min^{-1}$.

Thermal conductivity

The thermal conductivity of the blend [CH/(PVP-co-VAc)] film and $CaCO_3$ 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 in the determination of thermal conductivity in order to quickly reach steady state.

Water absorption

Swelling behavior of the blend [CH/(PVP-co-VAc)] film and $CaCo_3$ 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 were eventually weighed. Weight gain of the samples was recorded 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.

$$\text{Weight gain\%} = [(W_2 - W_1) / W_1] \times 100\% \qquad (1)$$

where W_2 is the weight of the wet sample at time t after swelling and W_1 is the weight of the dry sample before swelling.

Antibacterial properties

The Staphylococcus aureus (Staph.) and Escherichia coli (E.coli) microorganisms by disk diffusion method in accordance with the procedure described by Hwang and Ma. The method is a mean of measuring the effects of an antimicrobial agent on bacteria growth in a culture.

Results and discussions

FTIR Analysis

Fig.1 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 CH2 respectively. A peak observed at 1718.20 cm^{-1}, 1623.22 cm^{-1} indicates the presence of C=O stretching in secondary amide and N-H bending respectively. These peaks confirm the blending of (PVP-co-VAc) and chitosan [13]. From the FTIR spectrum of $CaCO_3$ nanoparticles illustrated in Fig. 1, it can be seen that the nano $CaCO_3$ had bands at 1868–1890 cm^{-1}, corresponding to the vibration mode of C–H of stearic acid, and also 809 and 1101 cm^{-1}corresponding to the in-out-plane bending and asymmetrical stretching vibration peaks of O-C-O, respectively. They all are characteristic peaks in calcite [14, 15].

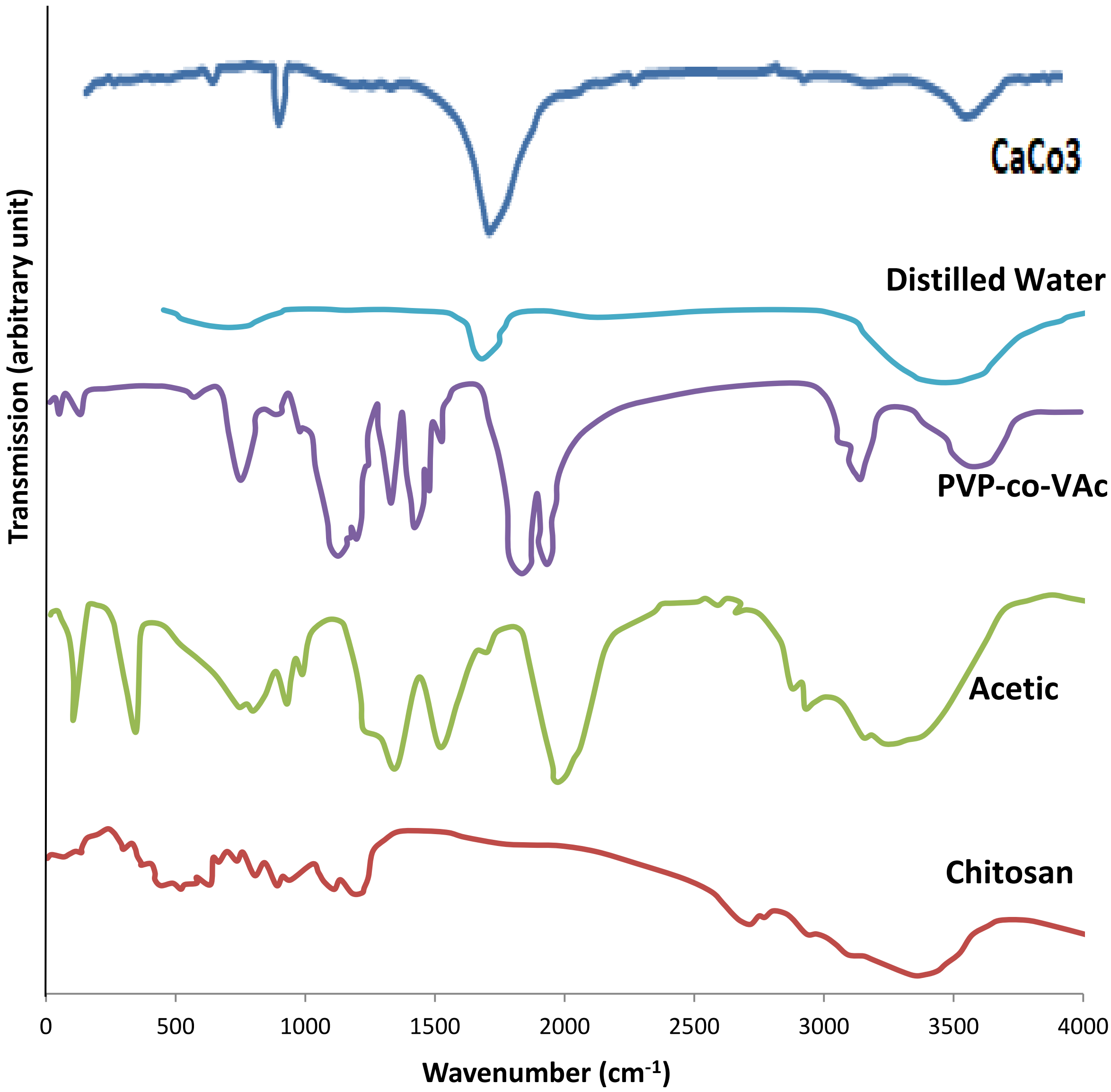

Fig.1: FTIR spectra of pure components.

Fig.2 shows the FTIR spectra for blend CP, A3, and A5 nanocomposites. The broadening of the band associated with the hydroxyl group revealed the creation of intermolecular hydrogen bonds. Simultaneously, a little move of the carbonyl stretch of (PVP-co-VAc) happened in the blends compared to the pure copolymer. In addition, the shifts proposed the creation of intermolecular hydrogen bonding. The low intensity of blend peaks (1245, 1670 & 3436) as shown in Table 2 may be due to that the incorporated inclusions strongly 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 attributed to overlapping effect, from the introduction of a large number of nano bonds [16]. These assignments of vibrational modes of the blend and nanocomposites bands are listed in Table 3.

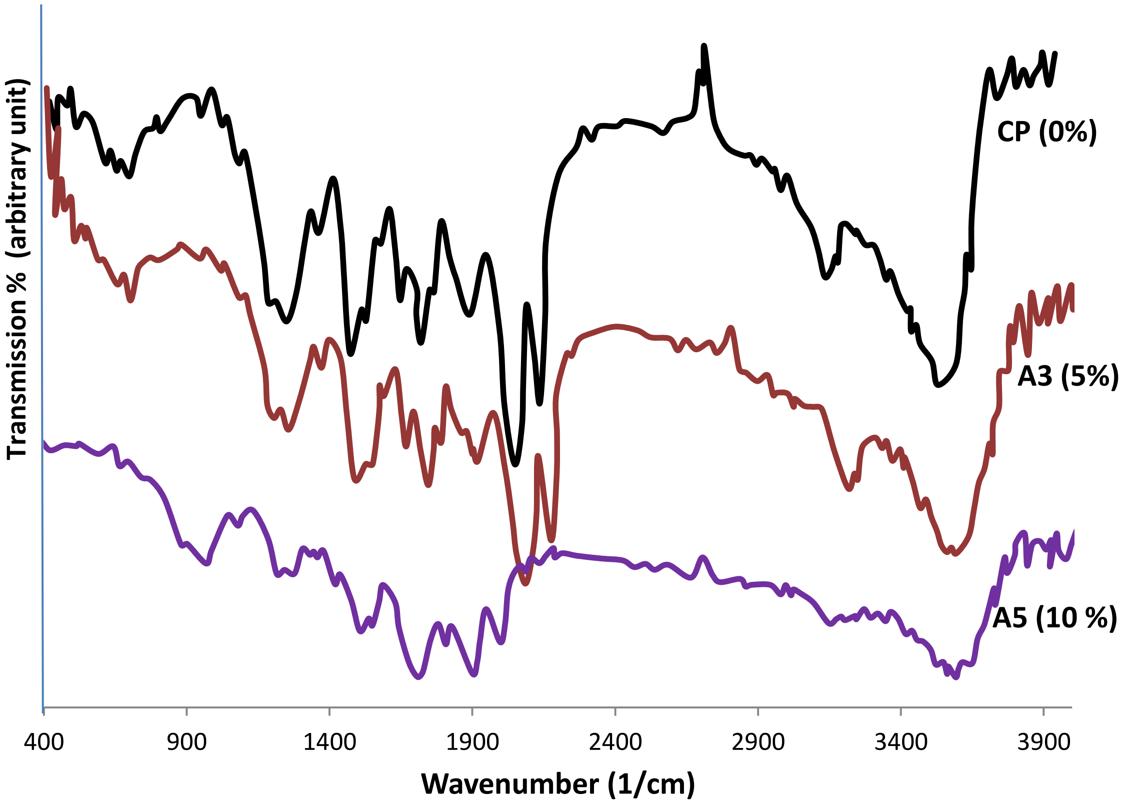

Fig.2: FTIR spectra for polymer blend (CP) and (A3 & A5) nanocomposites.

Table 2: Peaks position in the blend CP and nanocomposite (A3 & A5).

Peak No.	CP	A3	A5
1	435	493	437
2	649	648	665
3	898	844	894
4	1080	1080	1080
5	1245	1244	1244
6	1425	1427	1421
7	1670	1670	1676
8	1737	1735	1735
9	2921	2920	2867
10	3436	3446	3446

Table 3: Assignments of vibrational modes of blend and nanocomposites.

Description of vibrations mode	Wavenumbers (cm^{-1})	Ref.
O-H stretching	3000-3600	[15]
C=O stretching	1660-1730	[17]
CH_3 & C-H stretching	1372-1735	[18]
C-O- C stretching & O-CH_3 symmetric stretching	1000-1300	[19]
N-H stretching	3100-3500	[19]
The symmetric rocking of CH_2 & C–H bending wagging vibration	702 – 952	[20]
O-C-O asymmetrical stretching vibration	1418-1425	[21]

Tensile properties

The tensile test supply a signal of the strength and elasticity of the nanocomposites. Chitosan exhibits a poor mechanical strength and a strongly hydrophilic which makes it a poor candidate for food packaging. Blending [CH([PVP-co-VAc)] enhanced tensile strength, the results indicate that nanocomposite films with nano $CaCo_3$ shows a good tensile strength and young modulus than the blend film in A2 and A3 (3.5, 5 wt %). It was found that addition of $CaCO_3$ nanocomposite into the blend film could enhance the physical properties and mechanical properties of the film if the nanoparticle was added by a small percentage such as 3.5, 5 wt %. Fig.3 shows the stress-strain curve for blend and nanocomposite films, it was clear that the nanocomposite has a higher strength in A2 & A3 and less elongation for all the nanocomposite compared with blend film.

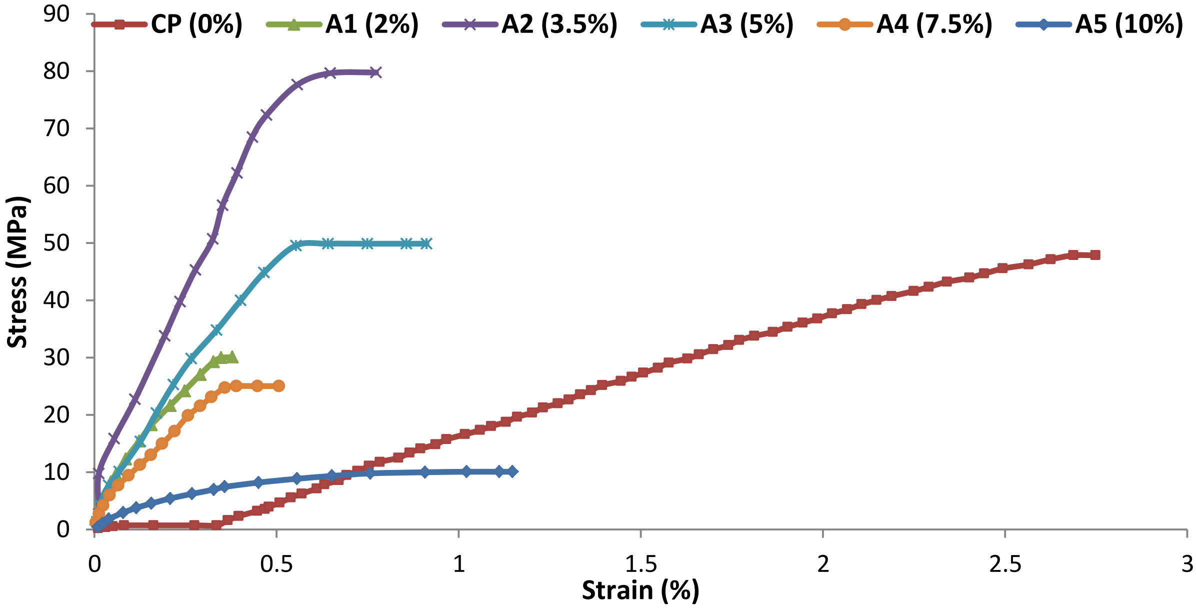

Fig.3: Stress-strain curves for the blend (CP) and nanocomposite (A1, A2, A3, A4, and A5) films.

The various amount of $CaCO_3$ (2, 3.5, 5, 7.5 and 10 wt.%) was conventionally added to the [CH/(PVP-co-VAc)] solution. As depicted in Fig.4, we notice that addition of $CaCo_3$ nanoparticles to the [CH/(PVP-co-VAc)] blend could enhance the physical properties and mechanical properties of the film because nanoparticles have a significant surface area to volume ratio effects. The results mention that nanocomposites have elevated tensile strength than blend film in (A2 & A3) the other nanocomposite have lower tensile strength than the blend film as listed in Table 4. Higher filler content may be lead to a poor distribution of filler across the matrix which caused the stress in the continuous phase to increase and promote poor tensile strength, the decrease in tensile strength can be explained by the imperfect distribution of the filler through the polymer matrix [22-24].

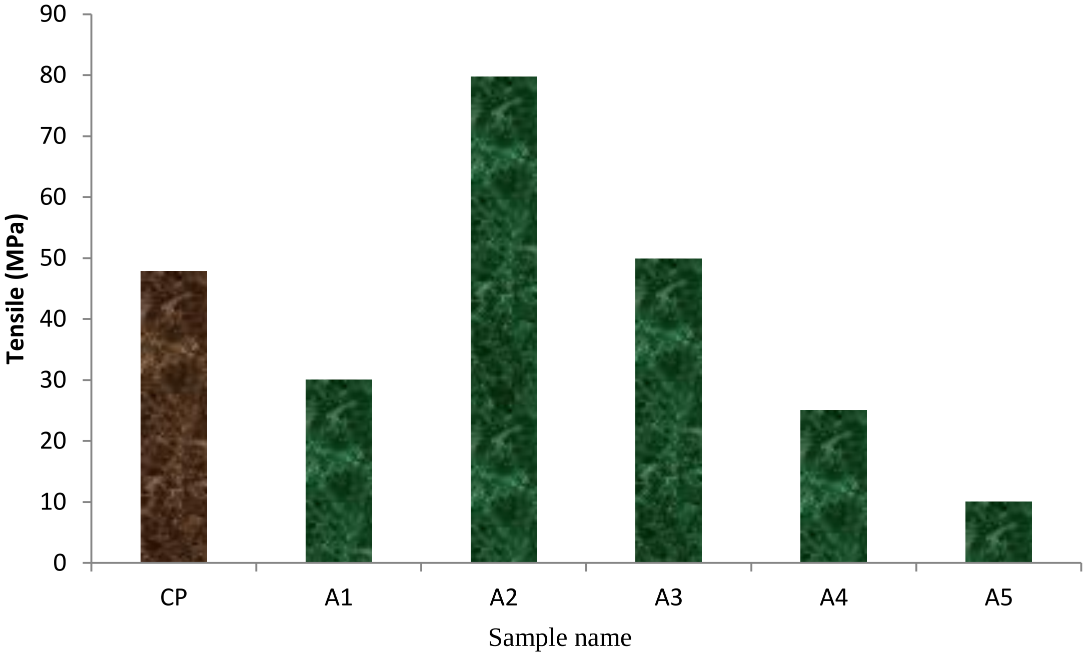

Fig.4: The Tensile strength of the blend and nanocomposite films.

Table 4: Properties of the blend [CH/(PVP-co-VAc)] and the $CaCO_3$ nanocomposites films.

Sample	Tensile (MPa)	Elongation %	Young modulus (MPa)
CP	47.87	2.746	1787
A1	30.06	0.37	9235
A2	79.75	0.77	1358
A3	49.87	0.91	7238
A4	25.02	0.5	6470
A5	10.07	1.14	1811

The mechanical properties of the blend (CP) and nanocomposites (A1, A2, A3, A4 & A5) are a result of the polymer conformation and the attraction energies (electrostatic attraction, van der Waals forces, and hydrogen bonding) between the chitosan and (PVP-co-VAc) chains [25, 26].

Thermal conductivity

The results of thermal conductivity of blend (CP) and $CaCO_3$ nanocomposite films show that the highest values of thermal conductivity were achieved in the blend film and it shows that the nanocomposites films had a lower thermal conductivity than the blend film as shown in Table 5 & Fig. 5.

Table 5: The thermal conductivity of blend (CP) and $CaCO_3$ nanocomposites.

Sample name	CH/[PVP-co-VAc]	$CaCO_3$ %	K (W/m.K)
CP	1:1	0	0.106760849
A1	1:1	2	0.076578391
A2	1:1	3.5	0.059625023
A3	1:1	5	0.062439777
A4	1:1	7.5	0.054047352
A5	1:1	10	0.053928299

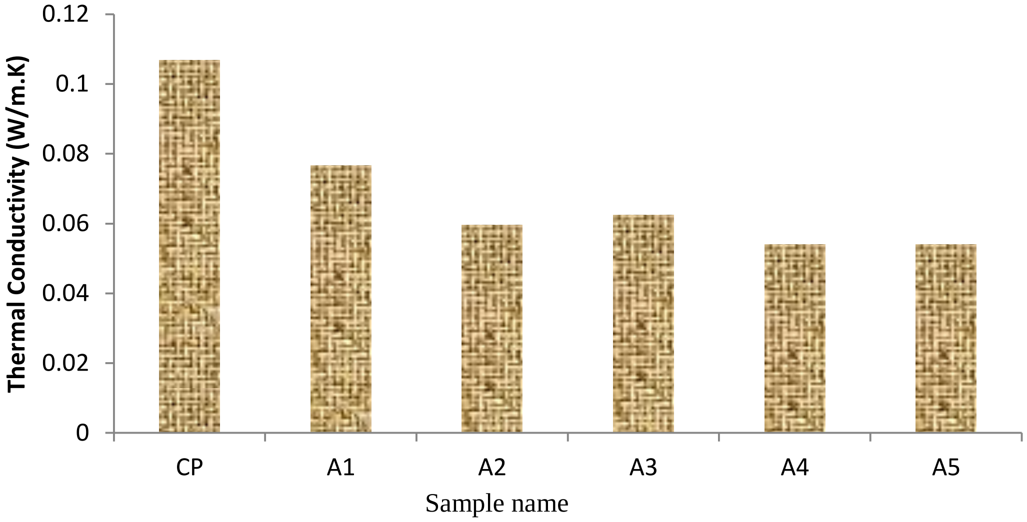

Fig.5: The thermal conductivity of (CP) blend and (A1, A2, A3, A4, and A5) nanocomposite films.

Thermal conductivity of nanocomposites depends on the thermal conductivity of the filler and matrix and the weight percentage of the filler, Moreover, the filler/matrix interface plays an important role in thermal conductivity of the blends, since the conductance of the heat in non-metallic materials occurs by the flow of polymeric chains vibration energy or phonons, along the temperature gradient in the material, therefore, for a two-phase system, interfacial contact between phases is very important, because phonons play an important role especially at low temperature and are very sensitive to surface defects at the interface. The thermal conductivity of these composite materials depends on several factors, first of all on the filler concentration, the ratio between the properties of the components, the sizes and the shapes of the filler particles. Small particle size has the large surface area that means large thermal interface resistance. The decrease of the filler size significantly increases the surface-to-volume ratio (S/V) which in turn increases the phonon scattering at the interfaces [20, 27].

Water absorption

The swelling behavior of the polymer blend and nanocomposites films loading in distilled water at ambient temperature is shown in Fig.6. One can observe from the plot, the character of swelling curves changes over time.

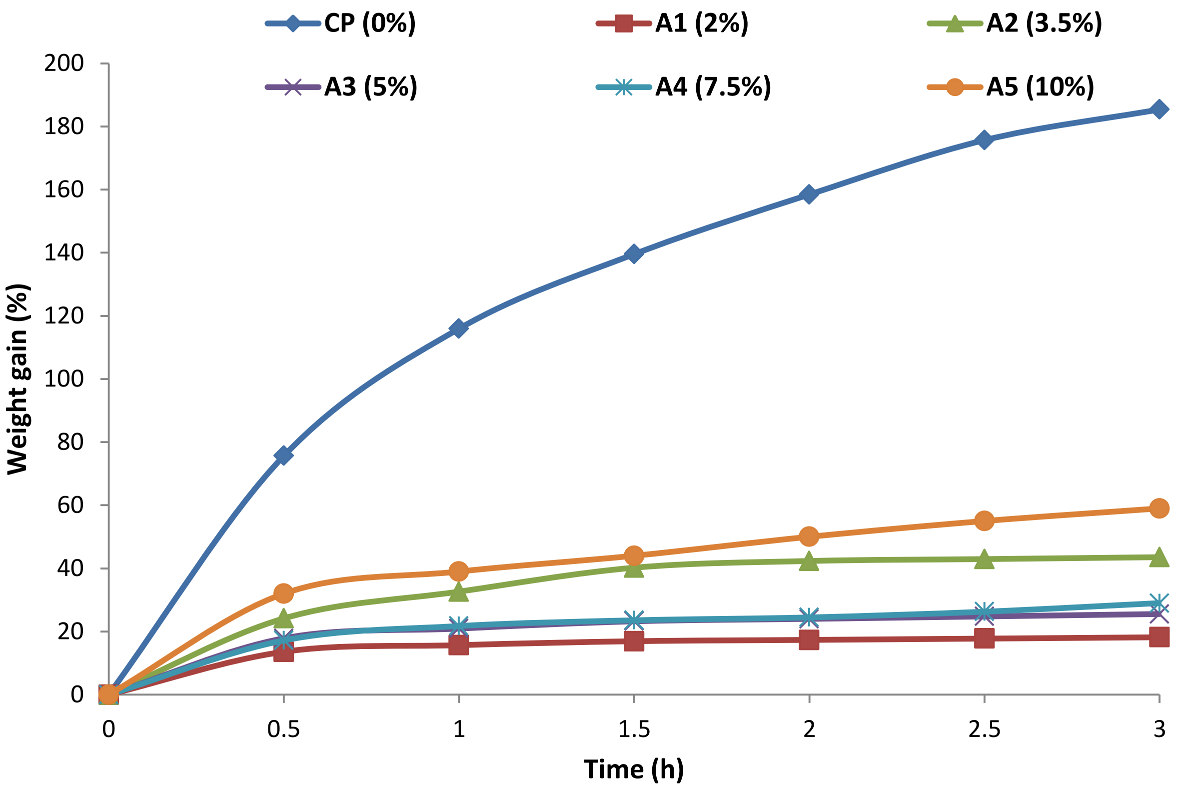

Fig.6: Effect of $CaCO_3$ content on swelling behavior of blend film (CP) and nanocomposites (A1, A2, A3, A4 & A5) at various interval time; (0.5,1, 1.5, 2,2.5, & 3 h).

The water absorption of the blend film was the highest among the other films because CH is elevated the hydrophilicity due to its hydroxyl groups (OH) and amino groups (NH_2) whereas for (PVP-co-VAc) only rely upon hydroxyl groups (OH). Consequently, hydroxyl group can shape robust hydrogen bonds with water (H_2O) than an amino group, while The water gain of the nanocomposites are minimize the [CH/(PVP-co-VAc)] blend as a result of contain $CaCO_3$ nanoparticles lowering nanoparticle is dispersal through the polymer and are capable to deny moisture [28, 29].

Antibacterial properties

Fig.7 shows photograph illustration of created inhibition zones of both E.coli and Staph for the blend (CP) and nanocomposites (A3 & A5). The results of antibacterial activity of [CH/(PVP-co-VAc)] blend and Nanocomposites are depicted in Table 6. It is shown that the inhibition zone in the nanocomposite was higher than for the blend. It is also observed that the inhibition zone for Staph was greater than that for E.coli.

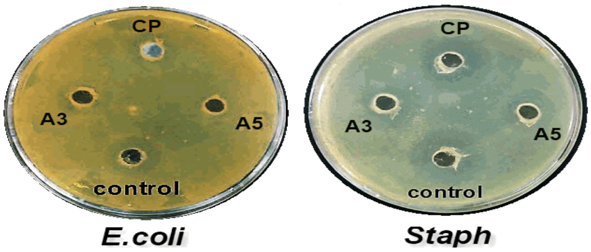

Fig.7: A schematic illustration of created inhibition zones of both E.coli and Staph for the blend (CP) and nanocomposites (A3 & A5).

Table 6: Average inhibition zone for [CH/(PVP-co-VAc)] blend and Nanocomposites.

Sample name (nano %)	**Inhibition zone (mm)**	
	E.coli	**Staph**
Control	15	24
CP (0 %)	12	16
A3 (5%)	15	21
A5 (10%)	-	16

Films with antimicrobial activity could help control the growth of pathogenic and spoilage microorganisms. An antimicrobial nanocomposite film is desirable because of its acceptable structural integrity and barrier properties imparted by the nanocomposite matrix, and the antimicrobial properties contributed by the natural antimicrobial agents. Materials in the nanoscale range have a higher surface-to-volume ratio when compared with their microscale counterparts. This allows nanomaterial to be capable to bind more copies of biological molecules, which confers greater efficiency [30,31]. This antibacterial activity can be imputed to the antibacterial effect of the nanoparticle. It is proposed that it may affect all membrane of the bacteria and so prevent their growth. It was found that blend and nanocomposite react with cell walls and cytoplasm membrane of E.coli, resulting pit in the cell wall of bacteria, and finally killing them.

Conclusions

Incorporation of the $CaCo_3$ nanoparticle to the blend [CH/[PVP-co-VAc)] via solution casting method produced the $CaCO_3$ nanocomposite films. The immobilized $CaCO_3$ exhibited a good distribution in chitosan film when the small amount of $CaCO_3$ was added. The results show that the tensile strength and Young's modulus of these nanocomposites were 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 $CaCo_3$ nanocomposites will be promising sources for photocatalyst materials for various organic compounds in the environment.

Acknowledgments

The authors would like to appreciate the chairing and administering of physics department for providing the necessary facilities, and thanks to the Material Science research group.

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