ฟิล์มคอมพอสิทไคโตซานที่มีการเติมอนุภาคเกาลินเพื่อเป็นสารดูดซับเอทิลีน
Kaolonite -Filled Chitosan Composite Films as Ethylene Absorbent

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บทคัดย่อ

ในงานวิจัยนี้ได้ทำการเตรียมฟิล์มคอมพอสิทไคโตซาน ที่มีการเติมอนุภาคเกาลินและศึกษาสมบัติการเป็นฟิล์มบรรจุภัณฑ์ยืดอายุการเน่าเสียของอาหาร โดยการทดสอบสมบัติการดูดซับเอทิลีนของฟิล์ม ฟิล์มคอมพอสิทไคโตซานถูกเตรียมโดยวิธีหล่อแบบ โดยมีปริมาณอนุภาคเกาลินต่างๆ กัน คือร้อยละ 0.5, 1.0, 5.0 และ 10.0 โดยน้ำหนัก และมีการเติมกลีเซอรรอลในอัตราส่วนที่คงที่เพื่อเป็นสารช่วยเพิ่มความยืดหยุ่นให้ฟิล์ม ที่ปริมาณอนุภาคเกาลินเพิ่มขึ้นส่งผลต่อความแข็งแรงของฟิล์มโดยทำให้ฟิล์มมีความแข็งแรงเพิ่มขึ้น 15-30 เปอร์เซ็นต์ การเติมอนุภาคเกาลินปริมาณ 5 เปอร์เซ็นต์โดยน้ำหนัก ทำให้ให้ฟิล์มคอมพอสิทมีสมบัติการซึมผ่านไอน้ำดีขึ้นประมาณ 20 เปอร์เซ็นต์ เมื่อเทียบกับฟิล์มไคโตซาน และพบว่าสมบัติการดูดซับเอทิลีนก๊าซของฟิล์มคอมพอสิทมีค่ามากที่สุดที่การเติมอนุภาคเกาลิน 10 เปอร์เซ็นต์

Abstract

This research study on the preparation of chitosan-kaolin composite film and application as food packaging by testing ethylene absorbent properties. Chitosan-kaolin composite film was prepared by a casting method. The content of kaolin – loaded composite film was varied as 0.5%, 1.0%, 5.0% and 10.0% w/w. Glycerol with fix content was used as plasticizer. An addition of kaolin particles was affect on tensile strength of composite films. An increasing in kaolin content was increased film rigidity about 15-30%. At kaolin loaded content 5% w/w improved in water vapor barrier properties about 20% . An addition of 10%kaolin particles in composite film was found to highest in ethylene absorption properties.

Introduction

In the second part of the 20th century industry and science have developed a big number of petroleum-based plastics with excellent properties and many fields of applications. In the year 2002 41% of all plastics were manufactured for packing and 47% out of that were produced for packing of foodstuff [1]. Consequently, approximately 19 % of all plastics are manufactured for packing of foodstuff.

The disadvantage of most of the petroleum-based plastics is their non-degradability and that they are based on a non-renewable resource producing not only a growing waste problem but also an excess of carbon dioxide. Only in the last decade of the 20th century science and industry focused more on the development of non-polluting plastics.

As mentioned before at least 19 % of all plastics are produced for packing of foodstuff. Substitution of non-degradable plastics with degradable plastics could lead to a decrease of waste - origin from plastics - of about 19%.

One alternative to non-degradable petroleum-based plastics is to use bio-based polymers materials that are synthesised and degraded in nature. Chitosan are such materials. Chitosan is the deacetylated product of chitin being the major compound in exoskeletons of insects and crustaceans as well as –in minor amounts- in the cell wall of fungi and microorganisms. Chitosan form films and membranes that are slightly yellow, clean, tough and flexible with good oxygen barrier but poor water vapour barrier and as another advantage of chitosan the products are complete biodegradable.

In this work chitosan composite films by addition with kaolonite naoparticles to form composite film to make films more water-resistant by introducing a hydrophobic surface. Furthermore, glycerol is used as plasticizer because it has a great ability to plasticize chitosan films and it is readily available.

After production of films they are characterised for their physical and chemical properties. Film characterisations for microscopic surface structure were performed using SEM, respectively. While surface properties including the contact angle of water on film surface, tensile properties and moisture absorption were evaluated according to the standard test methods.

MATERIALS AND METHODS

Materials

Chitosan was purchased from Ebase Co.,Ltd. (Thailand) as commercial grade with 80 Degree of Deacetylation and 250 kilodalton. Glycerol used as plasticizer in this film was purchased from Merk KGaA Darmstadt Germany. Kaolin powder Cas#1332-58-7 was purchased from China. Others reagent used are analytical grade.

Chitosan film and chitosan-kaolin composite film Preparation

The mixture of chitosan solution (1% w/v) , glycerol (1.0 g) and a various amount of kaolin particle (0.5, 1.0, 5.0 and 10.0 % w/w of chitosan) was slowly added to chitosan solution 100 ml at room temperature under stirring and stirring maintained at this condition for 3 h to completely mixting. After that , the mixture was maintained for 10 min before pour into acrylic mould with size 0.5 cm(height) X 24 cm(length) X 14 cm(width) and allowed to dry at room temperature.

Characterisation

Scanning electron microscopy (SEM)

Specimens were taken from chitosan and chitosan-composite films. Specimens were cut into dimension of ca. 5x5mm and mounted on stub with double-sided adhesive tape and coated with a thin layer of gold prior testing. SEM micrographs were taken using JEOL scanning microscope with an accelerating voltage of 10 kV and a magnification of 500 times the actual size.

Tensile properties

Tensile properties of chitosan and chitosan-composite films were determined using Lloyd testing machine according to ASTM D882 standard [15]. For the determination of tensile properties of chitosan and chitosan-kaolin composite films tensile strength was investigated. Five specimens were taken from every film and cut into dimension of 200x 15mm and conditioned for 24 hours at 25ºC and 55% RH prior testing.

Water vapor barrier property of chitosan film and chitosan-kaolin composite films

Water vapor permeability of all films was tested at 250C, 50%RH according to ASTM E398-03 using a water vapor transmission rate testing unit (Mocon model 398, USA) Three measurements were taken for each sample and the data were averaged to obtained an mean value.

Ethylene gas determination

Ethylene gas analysis was carried out using a Chrompack CP9001 (Middelburg, the Netherlands) fitted with a split/splitless injector and flame ionization detector (FID). Helium (99.999%, Sabalan, Tehran, Iran) was used as the carrier gas, the flow rate of the carrier gas was 0.5 mL/min for the first 30 s, increased up to 1.5 mL/min until the run time of GC was finished. The reduction of ethylene value obtained by the following equation;

$$\text{Rate reduction of ethylene gas} = \frac{\text{free volume} \times \text{ppm ethylene measure}}{\text{sample wt} \times \text{sealed time}}$$

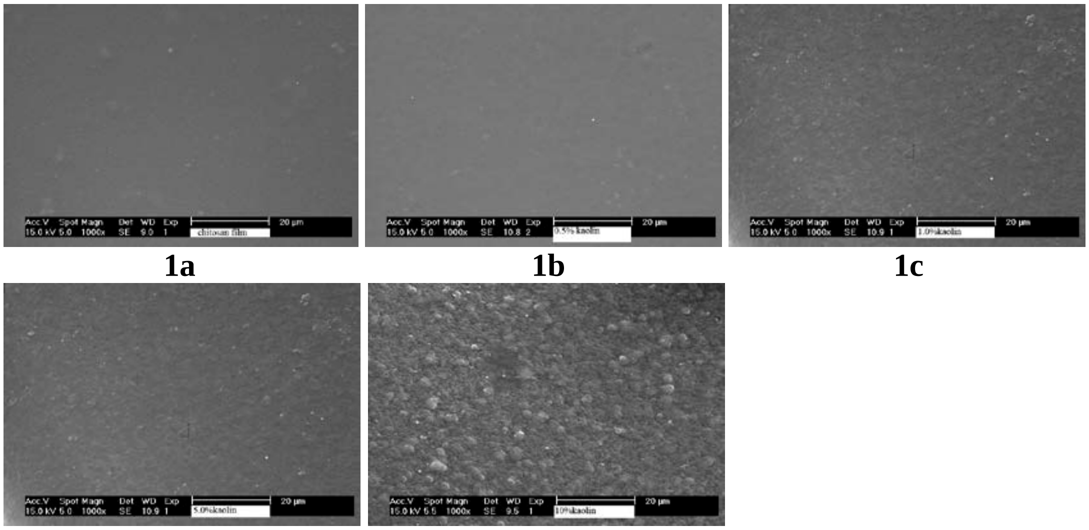
RESULTS AND DISCUSSION

Chitosan and Chitosan-Kaolin Composite Films

The obtained chitosan and chitosan-kaolin composite films were successful prepared using sovent casting method with transparent and slightly yellow. Chitosan-kaolin composite film with an addition of 10% kaolin particles was showed in roughness of film. From SEM micrographs chitosan and composite film with an addition of kaolin particles less than 10% were showed a smooth and homogeneous films (Fig 1a-d), while the composite film with 10% kaolin particles was slightly roughness(Fig 1e).

Table 1.Compositions of chitosan and chitosan-composite films formulation

Code of films	chitosan (g)	Kaolin (mg)	Glycerol (g)	Gracial acetic acid (ml)	Water(ml)
1	1	0	1	1	100
2	1	0.5	1	1	100
3	1	1.0	1	1	100
4	1	5.0	1	1	100
5	1	10.0	1	1	100



1a 1b 1c

1d 1e

Fig. 1 SEM micrographs at 1000X magnification of chitosan and chitosan-composite films

Table 2 Tensile strength , Water vapor transmission, and Ethylene absorption of films.

Films	**Tensile strength (MPa)**	**Water vapor transmission rate (g/m^2day)**	**Ethylene gas reduction ,% (after 8h)**
Chitosan film	44.0	860	0.23
0.5%kaolin composite film	37.4	845	0.20
1.0%kaolin composite film	32.3	760	0.19
5.0%kaolin composite film	17.3	745	0.17
10%kaolin composite film	16.2	730	0.14

Tensile properties of chitosan and chitosan-kaolin composite films

Tensile strength of chitosan and chitosan-kaolin composite films (0.5%, 1.0%, 5.0% and 10% kaolin) were 44.0 MPa for chitosan film and for chitosan-kaolin composite films resulted in 37.4, 32.3 17.3 and 16.2 MPa respectively.

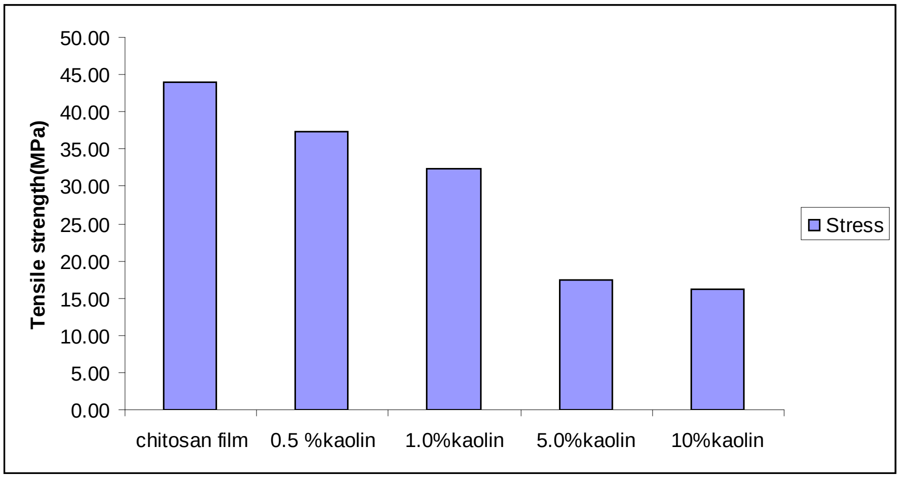


Figure 2 showed tensile strength of chitosan and chitosan-kaolin composite films

Water vapor barrier property of chitosan and chitosan-kaolin composite films

Water vapor permeability of chitosan film and chitosan-kaolin composite films were determined at condition of 25^0C, 50%RH. The water vapor permeability value of 860 g.mil/m^2.day.atm at 25^0C was found for chitosan film while chitosan-kaolin composite films indicated in range of 730-845 g.mil/m2.day.atm. This result indicated that an addition of kaolin particles not effect in water vapor barrier property by this condition (25^0C, 50%RH).

Ethylene absorption properties

An addition of kaolin particles into Chitosan film and chitosan-kaolin composite films was found to reduced ethylene concentration in chamber. The reduction in an initial ethylene concentration 35 $\mu L.L^{-1}$ in the chamber was determined overtime. An addition of 10%kaolin particles in composite film was found to highest in ethylene absorption properties.

Conclusion

The incorporated of kaolin particles into chitosan film as ethylene absorber in food packaging was found to reduced in ethylene gas in the chamber with the highest value of reduction was found 10% of kaolin particles was added. The reduction in tensile strength of composite films was showed to reduced film rigidity about 15-30%.

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