

# Environmentally Effective Biodegradable and Antimicrobial Properties of Biowaste Chitosan-Polyvinyl Alcohol Hydrogel Composite Film

Aung Than Htwe

**Abstract**— In the present investigation an ecofriendly approach and a simple homogeneous solution casting method led to the development of biodegradable chitosan/polyvinyl alcohol hydrogel composites. Various ratio of CS-PVA blended films are prepared and characterized by its physicochemical properties, water uptake ability, swelling property and thermal analysis. As a physicochemical result of good tensile strength and elongation at break of chitosan have been largely improved by adding PVA. The Water uptake ability of CS-PVA blended film was significantly increased with increasing amount of PVA. For a given blend composition, the degree of swelling mostly increased with longer immersion time. According to TG-DTG analysis, thermal stability of CS-PVA blended film was found to be slightly decreased than others. Consequently, the biodegradable nature of the CS-PVA blended film may appear after for a long time duration by using burial method. The property of various types of CS film, PVA film and CS-PVA blended film were tested on antimicrobial activity using agar disc diffusion method. From these results, all of the prepared CS film and CS-PVA blended film showed effective antimicrobial activities. If CS-PVA blended film can be widely used as packaging material instead of plastic bags, the environmental pollution can also be reduced.

**Keyword:** CS-PVA , water uptake, thermal analysis, biodegradable, antimicrobial test, packaging material

## 1. INTRODUCTION

Plastic waste becomes a serious problem because of its low weight-to-volume ratio and its inalterability over very long time duration. Today, incineration is a common method to get rid of polyolefines, but this unfortunately leads to high emission of carbon dioxide. One approach for solving this problem is to use biodegradable materials instead of non-renewable polymers, *e.g.*, in packaging. These materials have the potential to reduce environmental pollution by lowering solid disposal waste and reducing the need for incineration.

A number of natural polymers are being employed as biomaterials. Naturally occurring polymers include collagen, chitin, silk, alginate, starch, and elastin. Natural polymers offer the advantage of being similar to macromolecular substances, which the biological environment is prepared to recognize and to deal with metabolically. Problems associated with the stimulation of chronic inflammatory reaction and toxicity by synthetic polymers are largely suppressed or eliminated by using natural polymer. On the other hand, natural polymers are frequently quite immunogenic. Another attractive characteristic of natural polymers is their ability to be degraded by naturally occurring enzymes, implying that the implant will be degraded and eventually metabolized by physiological mechanisms. Thus, useful properties can be obtained by blending natural and synthetic polymers [1].

The industrial development of new polymers is expected to be rather limited in the future and blending of existing polymers will probably be the most effective way to design new polymeric materials with the desired combination of properties.

• *Dr, Demonstrator, Department of Chemistry, University of Yangon, Myanmar, Ph:09-9-57309102, Email:aungthanhtwe76@gmail.com*

The natural biopolymer, Chitosan [ (1 →4) -2- amino -2- deoxy-β - D - glucan ] is a natural aminopolysaccharide derived from N- deacetylation of chitin [(1 →4) -2- acetamido -2- deoxy-β - D - glucose with alkali [2].

Chitosan is widely used in food and pharmaceutical industry and in biotechnology. Chitosan polysaccharide has been extensively studied in the field of biomaterials and because of its biological properties, biodegradability, bioactivity and biocompatibility , it has attracted much attention .

Polyvinyl alcohol, PVA is a non-toxic, water -soluble synthetic polymer and has good physical and chemical properties and film - forming ability. The use of this polymer is important in many applications such as controlled drug delivery systems, membrane preparation, recycling of polymers and packaging. Studies on the mechanism of dissolution and changes in crystallinity and swelling behavior of PVA and its physical gel-forming capability, have been carried out [3,4].

This research work is mainly concerned on preparing biopolymer blended film that combine a chitosan (CS) and polyvinyl alcohol (PVA), and this research intend to use of packaging materials and reducing the environmental pollution. The water uptake and swelling behavior of these films were determined by conventional method. The characteristics of the prepared CS, PVA and CS-PVA blended film were carried out by modern techniques such as TG-DTA. The biodegradable and antimicrobial activities of CS film and CS-PVA blended film were also investigated. Finally, the characteristics nature of CS-PVA blended film was investigated as food packing material.

## 2. MATERIALS AND METHODS

Commercial chitosan sample from shrimp shell was purchased from Asian Technology Groups Co., Ltd., Local Industry, Yangon, Myanmar. Polyvinyl alcohol (Molecular

weight 20, 000, degree of hydrolysis 98%) was purchased from the British Drug House (BDH) Chemical Ltd, England. All other chemicals used were of analytical reagent grade. In all investigations, the recommended standard methods and techniques involving both conventional and modern methods were provided.

## 2.1 Preparation of Chitosan-Polyvinyl Alcohol (CS-PVA) Blended Film

Chitosan solution 1% w/v was prepared by dissolving 1g of CS in 100 cm<sup>3</sup> of 1% v/v acetic acid with often stirring for 30 minutes at room temperature to get a clear solution. Clear solution of PVA 2% w/v was put in autoclave for 20 minutes at 121° C and 0.1 MP a in water.

The prepared CS solution and PVA solution were mixed appropriate proportions to obtain a series of CS-PVA blends. The blends were prepared five different ratio of CS: PVA, (20:80, 40:60, 50:50, 60:40, 80:20 v/v) by thoroughly stirring the mixed polymer solution for about 30 minutes. The blended polymer solutions were kept for sufficient time to remove any bubble formation and were casted onto a cleaned and dried melamine plate at room temperature.

The melamine plates (6" x 4")size containing the blend solution were left for about 3 days to obtain CS-PVA blended films. The membranes after drying were removed easily from the melamine plates and were immersed in 1M NaOH solution to remove residual materials then washed with distilled water to remove alkali and unreacted materials and finally dried at room temperature [5].

## 2.2 Determination of Physicomechanical Properties

The tensile strength, elongation at break and tear strength of the samples were measured on an Tensile testing machine (Hours field 5000E), Cutter (Wallace) at room temperature with the rate of moveable jaw 100mm / min according to JIS K 7127 (1987). At least three samples were measured and the average values were reported.

## 2.3 Determination of Water Uptake (%)

The films to be tested were cut into 1" x 1" size. The films were immersed in distilled water at room temperature for the specified period of time. The films were removed from distilled water in beaker, blotted gently with tissue paper, weighed, and then put back into beaker for the next measurement. The water uptake of different samples was calculated using the following equation .

$$\text{Water uptake (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \%$$

where,  $W_1$  is the weight of completely dried sample and  $W_2$  is the weight of swelled sample in the distilled water at room temperature for 1 to 4 hours. Each experiment was replicated for three times. The resulting data are presented in Figure 3.

## 2.4 Determination of Degree of Swelling

The films to be tested were cut into 1" x 1" size. The films were immersed in distilled water at room temperature for the specified period of time. The films were removed from distilled water in beaker, blotted gently with tissue paper,

weighed, and then put back into the beaker for the next measurement. The procedure was continued until no more water is absorbed. Based on these values, swelling (%) were determined. Each experiment was replicated for three times. The degree of swelling was determined according to the following relationship.

$$\text{Degree of swelling (\%)} = \frac{W_s - W_d}{W_s} \times 100 \%$$

where,  $W_s$  and  $W_d$  represent the weight of the films after and prior to immersion [6].

All the experiments were carried at room temperature. Finally, the equilibrium degree of swelling of the as-prepared films was also determined after immersion in water for 4 days. Each experiment was replicated for three times. The resulting data are presented in Figure 4 and 5.

## 2.5 Identification of Differential Thermalgravimetric Analysis (TG-DTA)

Thermal stability of the tested films was evaluated by a simultaneous TGA-DTA (DTG-60H) operated under nitrogen atmosphere. Chitosan film, PVA film and CS-PVA blended film samples of about 8 mg each were accurately weighed into solid aluminium pans without seals. The measurements were carried out at a heating rate of 20.0 kJmin<sup>-1</sup> and scanning from 40 °C to 600 °C. The techniques employed were in accordance with the company's catalogue. The TG thermogram profiles of all prepared films are shown in Figure 6,7 and 8.

## 2.6 Determination of Biodegradation by Soil Burial Test

Biodegradation of prepared films was determined by soil burial test examining the weight loss and morphology changes. The prepared films were cut into 2" x 2" dimensions. The films (ca. 0.16 g) were then accurately weighed and buried in soil at an depth of 5 cm. They were taken out from the soil at an interval of one week. At least three samples were measured and the average values were reported . Sample geometry on degradation was also recorded by photo in figure 9 .

## 2.7 Determination of Antimicrobial of CS and CS-PVA blended Test by Agar Disc Diffusion Method

The CS and CS-PVA blended films were tested with *Bacillus subtilis*, *staphylococcus aureus*, *Pseudomonus aeruginosa*, *Bacillus pumalis*, *Candida albican* and *E. coil* species to investigate the nature of antimicrobial activity.

After preparing the bacteriological medias, the dried films were placed on the agar with flamed forceps and gently pressed down to ensure proper contact. The plates were incubated immediately or within 30 min after incubation [7]. After overnight incubation at 37°C, the results are shown in Table 1 and Figure 10 (A) and (B).

## 2.8 Application of CS- PVA Membrane

Lettuce (*L.sativa*) was packed with CS-PVA blended membrane and was placed in refrigerator. They were taken out from the refrigerator at an interval of one week. Sample

geometry was also recorded by photos in figure 11 (A) and (B).

### 3. RESULTS AND DISCUSSION

#### 3.1 On the Aspect of Characterization of CS-PVA Blended Films

In this work, blends of CS and PVA have been prepared by the solvent exporting and solution casting techniques. The mechanical properties of the obtained films have been investigated. The thickness of the various CS-PVA blended films was in the range of 0.05 to 0.08 mm.

Figure 1 indicate the mechanical properties of CS-PVA blended film with various ratios. The blend films 40:60 and 20:80 systems showed a very close percent elongation at break and different tensile strength properties. But wide variation was observed in 50:50, 80:20 and 60:40 ratios of CS and PVA in both the properties. This effect can be explained from the fact that the blending of chitosan with PVA leads interpenetrating network between them with in a reasonable range of composition. Figure 1 also showed that the tensile strength was found to increase with chitosan content up to 80:20 (v/v) around 55.5 MPa. The percent elongation break slowly decreased with the ratio 20:80, 40:60, 50:50, 60:40 and 80:20 (%v/v) of CS - PVA concentration, the percent elongation value reached to 8.3%.

Thus, the tensile strength and % elongation values are flexible in the ratio of CS-PVA 80:20 %v/v concentration. It can be explained that the CS-PVA content 80:20 v/v ratio may be affective parameter relevant to the mechanical properties.

Figure 2 showed that the profile of tear strength versus CS-PVA blended concentration. It indicated that the tear strength of CS-PVA ratio film (40:60, 20:80) is progressively increased and then (80:20) is decreased. The 80:20 ratio of CS-PVA concentration is significantly decreased in value of 57.0 KN/m.

In can be concluded that the reasonable CS-PVA blended films for packaging material can be prepared 80:20 (v/v) of CS (1% w/v) and PVA (2% w/v) according to the physicochemical properties.

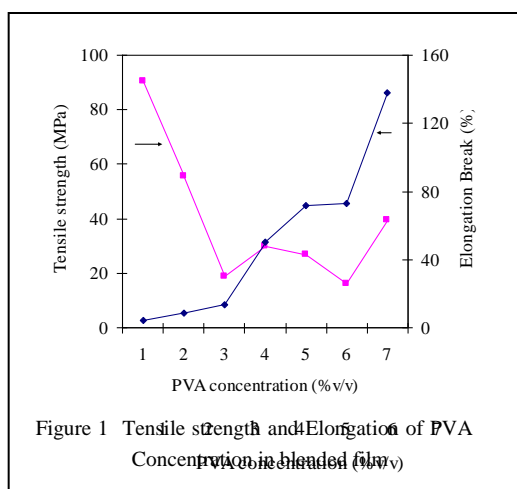


Figure 1 Tensile strength and Elongation of PVA Concentration in blended film

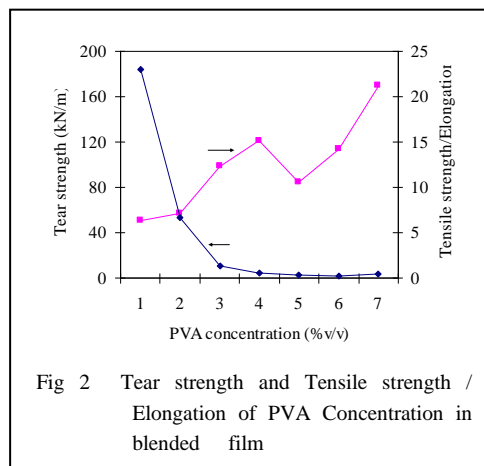


Fig 2 Tear strength and Tensile strength / Elongation of PVA Concentration in blended film

#### 3.2 Aspect of Water Uptake of CS-PVA Hydrogel Films

The degree of water uptake was investigated with increasing immersion time. The water uptake as a function of time for CS film and CS-PVA blended films were shown in Figure 3. The water uptake was one of the most significant parameter when a film to be used as packaging materials. The water uptake was the amount of water entrapped in the matrix including bound water.

As seen in figure 3, the water uptake of CS-PVA blended films were significantly difference as increasing percent of PVA solution. The lost of water from 1 hr to 3 hr was slightly difference and quite difference values in 4 hr for all prepared CS films. The water uptake may impart stickiness, tastiness and durability.

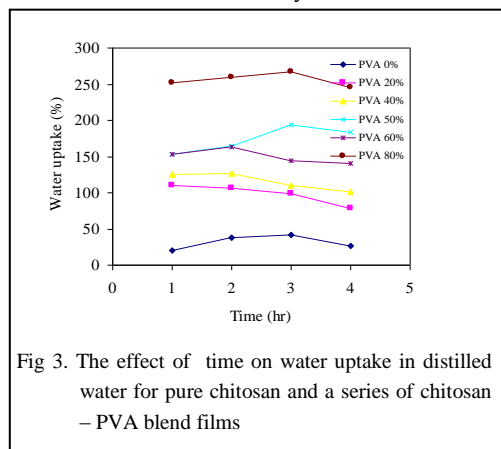


Fig 3. The effect of time on water uptake in distilled water for pure chitosan and a series of chitosan - PVA blend films

Figure 3

#### 3.3 Aspect of Degree of Swelling (%)

The degree of swelling of pure chitosan and a series of chitosan-PVA blended films with different blend compositions were shown in Figure 4 as a function of immersion time in distilled water at room temperature. For a given blend composition time, mostly the degree of swelling increased with increasing immersion time. With increasing chitosan content, the ultimate degree of swelling after 4 hours

of immersion time of CS-PVA blended films was found to increase *ca.*1 to *ca.*25 %, when CS content increased from 20 to 80 wt%.

The equilibrium degree of swelling (after 4 days of immersion time) for pure CS and a series of CS-PVA blended films as a function of PVA content was shown in Figure 5. Interestingly, the equilibrium degree of swelling of PVA film was increased with PVA content which was greater than that of pure CS film (*i.e.*, *ca.* 69% versus *ca.* 45 %). For CS-PVA blended films, the equilibrium degree of swelling was found to increase *ca.* 50 to *ca.* 69%, as a function of increasing PVA content.

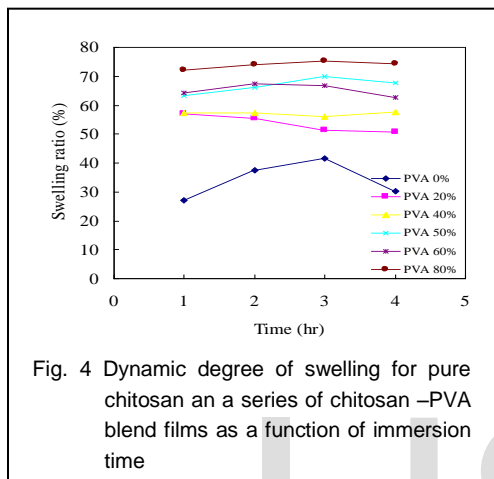


Fig. 4 Dynamic degree of swelling for pure chitosan and a series of chitosan-PVA blend films as a function of immersion time

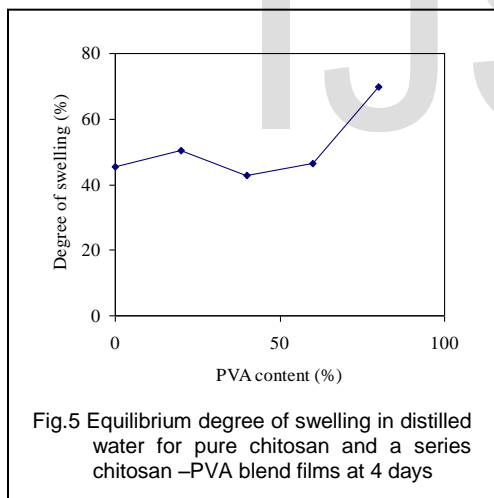


Fig.5 Equilibrium degree of swelling in distilled water for pure chitosan and a series of chitosan-PVA blend films at 4 days

### 3.4 On the Aspect of TG-DTG Analysis

Thermal stability of prepared chitosan film, PVA film, and CS-PVA film were investigated by TG-DTG analysis under nitrogen atmosphere and heating rate of 20 °C min<sup>-1</sup> from 40 to 600 °C. Figure 6,7 and 8 described the degradation peak values and weight loss of CS film, PVA film, and CS-PVA blended film.

According to the TG-DTG thermo gram profiles, CS film and PVA showed two decomposition stages and CS-PVA film gave four decomposition stages. All of the tested samples showed initial weight loss between 60 °C and 107 °C, likely a

result of moisture evaporation upon heating. The amount of moisture content in PVA film was lowest about 6% and CS film and CS-PVA film gave nearly 11 %. It can be suggested that interaction of water with CS film and CS-PVA blended film was stronger than PVA film. For PVA film, the broad exothermic peak at 177.80 °C was release of sorbet water and the degradation temperature at 294.89 °C presented uncoiling of polymer chain in some of the fraction of PVA chain. The pure chitosan film decomposed with a sharp weight loss nearly 300 °C and the rate of the decomposition reached 37.199 %. This degradation belongs to decomposition of chitosan molecule in chitosan film which agreed the literature values. The initial degradation temperature of 402.93 °C and 509.17 °C in TG-DTA profile of CS-PVA film showed quite degradation of pure components with mass change about 14 %. According to the degradation results, thermal stability of CS-PVA blended film was found to be slightly decreased to those of pure components.

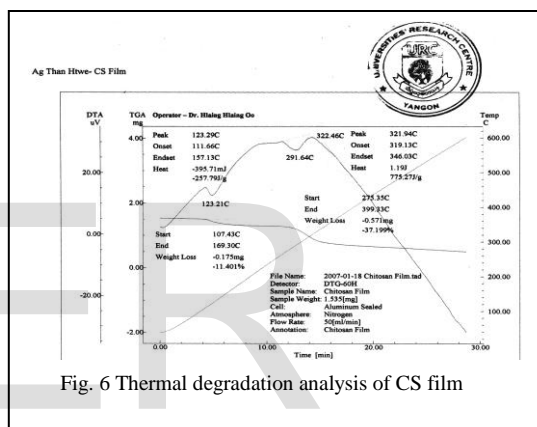


Fig. 6 Thermal degradation analysis of CS film

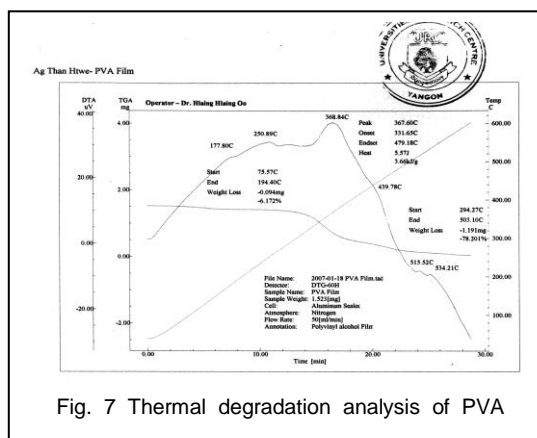


Fig. 7 Thermal degradation analysis of PVA



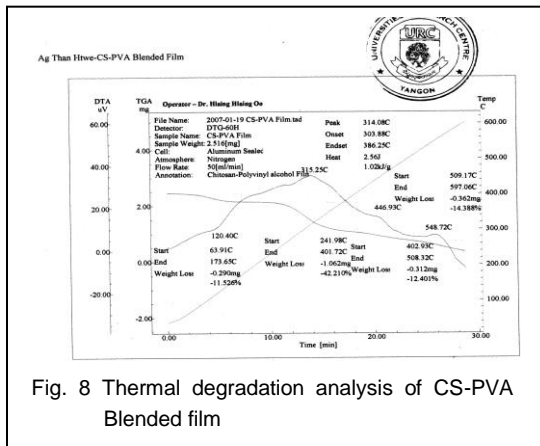


Fig. 8 Thermal degradation analysis of CS-PVA Blended film

### 3.5 On the Aspect of Biodegradation

In this work, bio-degradation of CS film, PVA film and CS-PVA blended film were tested by soil burial method. Soil burial is a traditional way to test samples for degradation because of its similarity to actual condition of waste disposal. Uniformly sized samples were buried in the soil. Figure 9 showed biodegradation nature of CS film, PVA film and CS-PVA film. This figures clearly showed that significant deformation of PVA film was found after two weeks although there was insignificant degradation of CS film and CS-PVA blended film. However, quite deformation of CS film and CS-PVA film appeared after 8 weeks. Therefore, the prepared CS-PVA blend film may be disappeared after for a long time duration by using burial method.

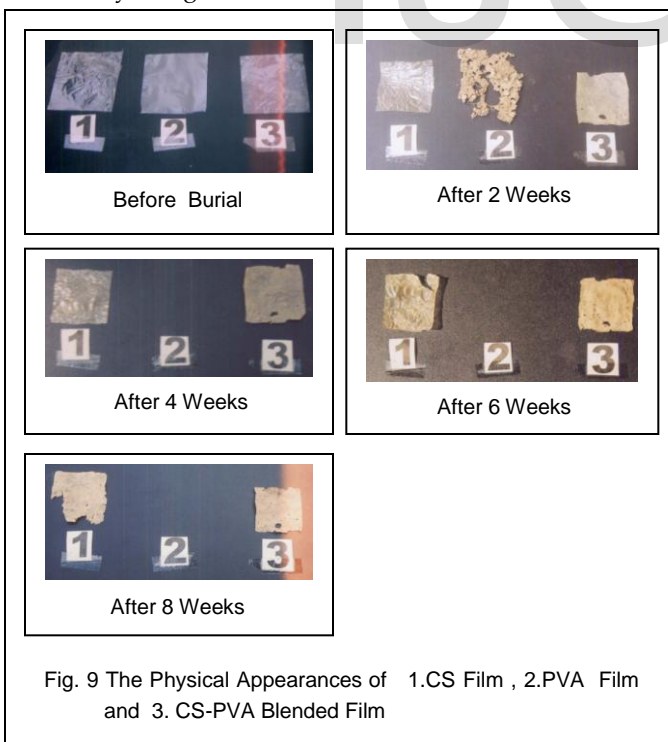


Fig. 9 The Physical Appearances of 1. CS Film , 2. PVA Film and 3. CS-PVA Blended Film

### 3.3.6 Antimicrobial Activity of CS Film and CS-PVA Blended Film

Antimicrobial activity of CS film and CS-PVA blended film are shown in Table 1. The tested films were 1%e w/v CS film and 80:20 CS-PVA (% v/v) blended film. Tested organisms were *Bacillus subtilis*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Bacillus pumilis*, *Candida albican* and *E.Coli*. As seen in figure 10, antimicrobial test of CS film and CS-PVA blended film were used the agar medium cultivation. According to the experimental results, the prepared CS film and CS-PVA film were really effective to antimicrobial activity.

TABLE 1  
Antimicrobial Activity of CS film and CS-PVA

No	Micoorganism	CS film	CS-PVA film
1	<i>Bacillus subtilis</i>	++	-
2	<i>Staphylococcus aureus</i>	++	++
3	<i>Pseudomonas aeruginosa</i>	++	+
4	<i>Bacillus pumilus</i>	++	++
5	<i>Candida albican</i>	++	++
6	<i>E-coil</i>	+++	++

+ = common, - = no reaction  
++ = porminent +++ = significant

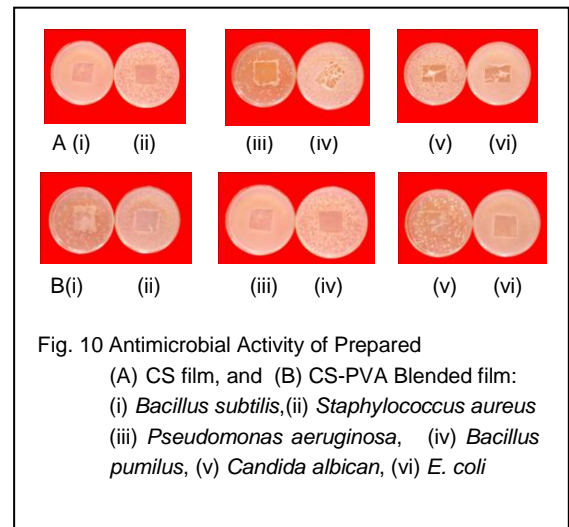


Fig. 10 Antimicrobial Activity of Prepared (A) CS film, and (B) CS-PVA Blended film: (i) *Bacillus subtilis*, (ii) *Staphylococcus aureus* (iii) *Pseudomonas aeruginosa*, (iv) *Bacillus pumilus*, (v) *Candida albican*, (vi) *E. coli*

### 3.7 On the Aspect of Application of CS-PVA Membrane

Plastic films are a family of modern, high performance materials which play an essential part in almost every aspect of our daily lives. Around 60 % of everything is packaged in plastic film because it is economical, high strength, low-weight protective barrier from carrier bags to cling film.

However, plastic films are based on oil or natural gas. Over the last decades, plastic waste becomes a serious problem because of its low weight-to-volume ratio and its inalterability over very long time duration. Today, incineration is a common method to get rid of polyolefines, but this unfortunately leads to high emission of carbon dioxide. One approach for solving this problem is to use biodegradable materials instead of non-renewable polymers, e.g. in packaging. These materials have the potential to reduce environmental pollution by lowering solid disposal waste and reducing the need for incineration. Chitosan is one of the materials to solve this problem. The prepared CS-PVA film is moisture retention activity and highly convenient for deepfreeze. Moreover, protection and preservation of products and other goods from damage, loss or spoilage. In addition, it is safe to handle and flexible. It is light weight as plastic film, non-toxic, and economical because of its resource is Prawn shell waste. The unique activity of chitosan is antibacterial and antifungal activity. Thus, it should be used to packaging material. Therefore, CS-PVA blended film was tested for comparison of protective and preservation property with commercial plastic film. Figure 11 (A) showed fresh condition of *Lactuca sativa* plant; Myanmar means Salatt and it was kept at outdoor storage. Figure 11 (B) clearly showed that packaging of Salatt with CS-PVA film was more fresh than others. The prepared CS-PVA blended film ensures that many foods remain hygienic, fresh and nutritious. Moreover, it also help reduce the amount of preservatives needed.

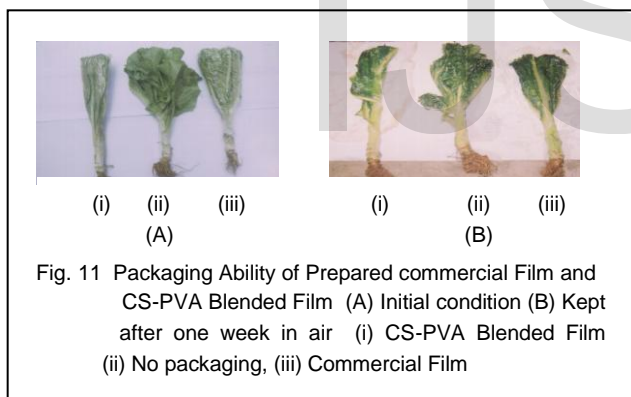


Fig. 11 Packaging Ability of Prepared commercial Film and CS-PVA Blended Film (A) Initial condition (B) Kept after one week in air (i) CS-PVA Blended Film (ii) No packaging, (iii) Commercial Film

#### 4. CONCLUSION

In this study, Blend membranes consisting of chitosan and PVA were prepared from the solvent casting technique. The chitosan-PVA and blended membranes were clear, flexible and transparent. The chitosan based various types of PVA blended films were prepared by blending, casting and by solvent evaporating technique under autoclaving conditions of 0.1 MPa in a time frame of 20 minutes. The various type of CS-PVA blended films were evaluated using different concentration of chitosan and polyvinyl alcohol. Mechanical properties of 80:20 and 50:50 systems are greater and showed very close % elongation at break and tensile strength. Due to the hydrogen bonding interaction that occurs between the

functional groups of CS and PVA, the physically cross-linked composite material is essentially insoluble in non acidic aqueous solutions.

The water uptake and swollen blend membrane has a higher degree of hydration, as measured by water uptake and swelling ratio, which can be altered by varying the weight percent of PVA in the membrane matrix.

From TG-DTG analysis, thermal stability of CS-PVA blended film was found to be slightly decrease than those of pure component CS film and PVA film.

The property of various types of CS film, PVA film and CS-PVA blended film were tested on its antimicrobial activities. The pure CS film and CS-PVA blended film were tested by six bacteria organisms using agar disc diffusion method. It can be noted that all of the bacteria agents come in contact with films the bacteria were killed. According to these results, the prepared CS-PVA blended film might be use as packaging for vegetables and food. This CS-PVA film ensures that vegetables and food remain hygienic, fresh, nutritious, and reduce amount of preservatives needed. It can also help prevent contamination and allow outdoor storage of goods.

#### ACKNOWLEDGEMENT

The author feel indebted to Professor and Head Dr. Hnin Hnin Aye, Department of Chemistry, University of Yangon, Yangon, Myanmar, for his stimulating suggestions.

#### REFERENCES

- [1] Correlo V.M., L.F Boesel, M. Bhattacharya, J.F Mano, N.M. Neves, R.L. Resis, "Properties of Melt Processed Chitosan and Aliphatic Polyester Blends", *Materials Science and Engineering A*, vol. 403, pp. 57-68, 2005
- [2] Mangala.E., T. Suresh Kumar, S. Baskar, K. Panduranga Rao, "Development of Chitosan/Poly (vinyl alcohol) Blend Membranes as Burn Dressings", *Trends Biomater. Artif. Organs.*, vol. 17, no.1, pp. 34-40, 2003
- [3] Bahrami S.B., S.S. Kordestani, H. Mirzadeh, P. Mansoori, "Polyvinyl Alcohol-Chitosan Blends : Preparation, Mechanical and Physical Properties", *Iranian Polymer Journal*, vol.12, no.2, pp.139-146, 2003
- [4] Peesan M., R. Rujiravanit, P. Supaphol, " Characterisation of Beta-Chitin/ Poly (Vinyl Alcohol) Blend Films" , *Polymer Testing* , vol. 22, pp. 381-387, 2003
- [5] Aung Than Htwe, Sandar Tun, Khin Aye May, Kyaw Myo Naing, "Studies on Preparation, Characterization and Application of pH-Sensitive Biodegradable Chitosan-Polyvinyl Alcohol Hydrogel", *Jour. Myan. Acad. Arts & Sc.*, vol. XI, no. 1, pp. 127-140, 2013
- [6] Wang T., M. Turhan, S. Gunasekaran, "Selected Properties of pH – sensitive , Biodegradable Chitosan – Poly (Vinyl Alcohol) Hydrogel", *Polym Int*, vol. 53, pp. 911-918, 2004
- [7] Aung Than Htwe, Sandar Tun, Khin Aye May, Kyaw Myo Naing, Hla Ngwe, "Some Physicochemical and Antimicrobial Properties of pH-Sensitive Biodegradable Chitosan-Polyvinyl Alcohol Hydrogel Films", *Universities Research Journal*, vol. 8, no.1, pp. 31-48, 2015

# IJSER