

## Investigation of Weight Loss Percent from Biodegradable Chitosan Composite Membranes by Soil Burial Test and TG-DTA Analysis

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### Abstract

The chitosan-alginate-starch composite membranes (CAS 1- 4), modified chitosan-alginate-starch-glycerol composite membranes (CASG 1- 4) and modified chitosan-alginate-starch-sorbitol composite membranes (CASS 1- 4) were prepared by using casting and autoclaving methods. These membranes have smooth surfaces, highly transparent and pale yellow colour. The mechanical properties such as tensile strength, elongation at break and tear strength of these prepared membranes were determined. Based on the mechanical properties of prepared composite membranes, CAS-3, CASG-2 and CASS-2 composite membranes were chosen as selected membranes due to their high tensile strength. The selected composite membranes (CAS-3, CASG-2 and CASS-2) were characterized by TG-DTA analyses. The biodegradable properties of these membranes were tested by soil burial method in sandy soil.

**Keywords:** composite membranes, mechanical properties, biodegradable properties

### Introduction

Chitosan is derived from chitin, a natural abundance substance found in the exoskeleton of insects, shells of crustaceans and fungal cell walls. Chitosan has been studied as biomedical material due to its wound healing effect, hemostasis, biocompatibility, biodegradability, antimicrobial activity, and so on. For these reasons, chitosan is biomedically very valuable material. It is generally soluble in acids although it has crystalline structure and several hydrogen bonds (Nagahama *et al.*, 2009). Chitosan has many physicochemical properties (reactive OH and NH<sub>2</sub> groups) and biological (biocompatible and biodegradable) properties that make it an attractive material used in various applications. These properties include: biodegradability, lack of toxicity, antifungal effects, wound healing acceleration, and immune system stimulation (Martino *et al.*, 2005). Because of its biological and chemical properties chitosan has the ability to bind to particular materials including cholesterol, fats, proteins, metal ions and even tumor cells. These allow chitosan to be used as a chelating agent in various applications (Foda *et al.*, 2007). Membrane obtained from chitosan of higher degree of deacetylation exhibited higher tensile strength and higher elongation at break. In addition, membranes cast from chitosan with 75% degree of deacetylation displayed higher permeability and higher water absorption (El-hefian *et al.*, 2011). Chitosan; a polysaccharide is derived from naturally occurring polysaccharide compound, viz chitin. One of the soluble properties of chitosan makes it attractive for many industrial and biomedical applications. According to its pH dependent solubility, it forms stable films on various surfaces under natural and basic pH condition (Koev *et al.*, 2010). Chitosan is a

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nontoxic, highly hydrophilic and has film forming ability. These advantages have made chitosan as membrane materials. With its free amine groups, the structure of chitosan can be modified easily in order to improve its properties for many industrial and biomedical applications (Tan *et al.*, 2002).

## Materials and Methods

### Sample Collection

Chitosan sample was purchased from Shwe Poe Co. Ltd., Hlaing Tharyar Township, Yangon Region.

Starch was prepared from maize grain, *Zea mays* L., this sample was collected from Insein market, Yangon Region.

### Preparation of Chitosan-Alginate-Starch (CAS) Composite Membranes

Chitosan-alginate-starch (CAS) composite membrane was prepared by following procedure. Firstly, chitosan 1.5 % (w/v) was dissolved in 1 % (v/v) acetic acid solution and stirred for 1 h to obtain the clear homogeneous chitosan solution. Secondly, sodium alginate 3 % (w/v) and starch solution 0.3 % (w/v) were prepared individually and then they are mixed and stirred for 30 min. Finally, chitosan solutions was added to these mixture solution and stirred for 1 h. The resulting prepared solutions were poured onto melamine plates and membranes were allowed to dry at room temperature for one week to obtain composite membranes. By using various ratios of starch 0.1 %, 0.2 %, 0.3 % and 0.4 % (w/v) prepared composite membranes were denoted as CAS-1, CAS-2, CAS-3 and CAS-4 respectively.

### Preparation of Chitosan-Alginate-Starch-Glycerol (CASG) Composite Membranes

Modified chitosan-alginate-starch-glycerol (CASG) composite membranes were prepared by using optimum ratios of 1.5 % (w/v) chitosan, 3 % (w/v) sodium alginate, 0.3 % (w/v) starch solution and 0.10 % (w/v) glycerol. The glycerol was also used as plasticizer for flexibility of membranes. The resulting modified composite solutions were autoclaved at a pressure of 0.1 MPa and  $121 \pm 1$  °C for 1 h. After that CASG composite membranes were prepared by using various percentages of glycerol 0.05 %, 0.10 %, 0.15 % and 0.20 % and prepared membranes were denoted as CASG-1, CASG-2, CASG-3 and CASG-4 respectively.

### Preparation of Chitosan-Alginate-Starch-Sorbitol (CASS) Composite Membranes

Modified chitosan-alginate-starch-sorbitol (CASS) composite membranes were prepared by using optimum ratios of 1.5 % (w/v) chitosan, 3 % (w/v) sodium alginate, 0.3 % (w/v) starch solution and 0.10 % (w/v) sorbitol. The sorbitol was also used as plasticizer for flexibility of membranes. The resulting modified composite solutions were autoclaved at a pressure of 0.1 MPa and  $121 \pm 1$  °C for 1 h. After that CASS composite membranes were prepared by using various percentages of sorbitol 0.05 %, 0.10 %, 0.15 % and 0.20 % and prepared membranes were denoted as CASS-1, CASS-2, CASS-3 and CASS-4 respectively.

### Mechanical Properties

#### Determination of Thickness

Thickness of the CAS, CASG and CASS composite membranes were measured by using NSK Micrometer. The thickness of the membranes were measured at 5 locations (center and 4 corners) using digital micrometer. The resulting data of all membranes was 0.10 mm.

### **Determination of Tensile Strength and Elongation at Break**

CAS, CASG and CASS composite membranes were cut off according to JIS K 7127 (1987) and the shape and dimension of test pieces were obtained. The both ends of test pieces were firmly clamped in the jaw of testing machine. One jaw was fixed and the other was moveable. The rate of moveable jaw was hold 100 mm/min. The resulting data was shown at the recorder. This procedure for tensile strength was repeated for three times. The resulting data are presented in Tables 1, 2, 3 and Figures 1, 2, 3.

### **Determination of Tear Strength**

The specimen was cut off by using die-cutting. Specimen cut with a single nick (0.05 mm) at the entire of the inner concave edge by a special cutting device using a razor blade. The clamping of the specimen in the jaw of test machine was aligned with travel direction of the grip in 100 mm/min. The order of the machine was showed the highest force to tear from a specimen nicked. The procedure was repeated three times for each result. The resulting data are described in Tables 1, 2, 3 and Figures 1, 2, 3.

### **TG-DTA Analysis**

Thermal stability of the tested membranes was evaluated by a simultaneous TG-DTA (DTG-60) operation under nitrogen atmosphere. Selected CAS-3, CASG-2, and CASS-2 composite membranes of about ~ 1.0 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 thermogravity profiles of all prepared membranes are shown in Figure 4 and resulting data are presented in Tables 4-6.

### **Determination of Biodegradation**

#### **Soil burial test**

Biodegradation was determined by soil burial test examining the weight loss and morphology changes. First, the membranes were cut into 1"× 1" dimensions. The membranes were then accurately weighed and buried in soil at the depth of 5 cm. Next, the buried membrane in the first hole was taken out after one day. The same is with the ones in the second, third, fourth, fifth, sixth, seventh and last holes were taken out after 2, 3, 4, 5, 6, 7, and 8 days respectively. The membranes were weighed again to investigate how much weight each one lost. After that, sample geometry on degradation was recorded by taking photo. The results are shown in Figures 5-7 and in Table 7.

#### **Analysis of soil**

The soil sample was obtained from waste disposal area. The soil sample was taken and dried in the shade. After all the soils had been dried, the sample was ground and sifted.

##### **(i) Determination of moisture**

Air dried soil of about 1g was accurately weighed in the porcelain dish and heated in oven at 105°C for three hours. This heating process was repeated to obtain a constant weight. The loss in weight was expressed in percentage.

##### **(ii) Determination of pH**

Air-dried soil (10 g) was accurately weighed and placed in a 50 ml shaking bottle, 25 ml of distilled water was poured and shaken vigorously for five minutes and left overnight. The pH of the soil solution was measured by using pH meter.

## Results and Discussion

### Aspect of Membranes Preparation

In the present work, the modified chitosan membranes were prepared by solution-casting from solution of chitosan in dilute acetic acid, sodium alginate solution and starch solution in various concentrations. In this process, chitosan was used as the base polymer. Chitosan as such does not have enough mechanical strength required for a wound dressing material, however, it has antimicrobial property as well as wound healing capacity. To give better tensile strength to the end product, sodium alginate and starch were added and to give flexibility to the composite glycerol and sorbitol were added. Both chitosan and sodium alginate have wound healing ability but their abilities were decreased when these two were mixed. Furthermore, starch solution was used to upgrade the healing ability. The gel was formed by chemical reaction when the sodium alginate was dissolving in water. The special property of alginates is the ability to form membranes of sodium alginate. The colour of the chitosan-sodium alginate-starch membranes are varied slightly to yellow with increasing chitosan content.

### Mechanical Properties

The mechanical properties such as tensile strength, tear strength and elongation at break are important parameters for showing the nature of membranes. The mechanical properties of CAS 1-4, CASG 1-4 and CASS 1-4 composite membranes are shown in Tables 1, 2, 3 and Figures 1, 2, 3. The more tensile strength of membrane, the higher elasticity of the membrane. This means to point out that CAS-3, CASG-2 and CASS-2 composite membranes indicated the more flexible and more elastic than the others.

**Table 1 Mechanical Properties of the Chitosan-Alginate-Starch (CAS) Composite Membranes Containing Various Concentrations of Starch**

Membrane	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kNm <sup>-1</sup> )
CAS- 1	12.50	19.00	68.00
CAS- 2	18.30	10.00	21.00
CAS- 3	19.50	38.00	32.90
CAS- 4	9.80	25.00	44.30

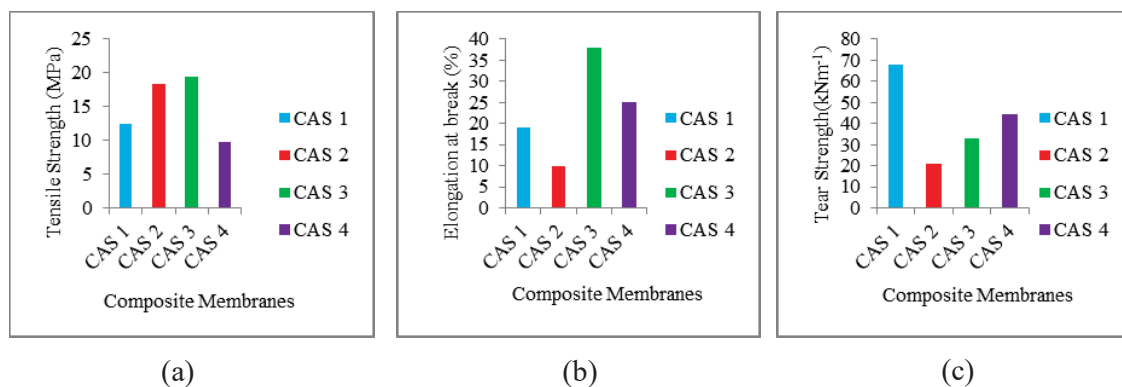
CAS- 1= Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.1 %) w/v

CAS- 2= Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.2 %) w/v

CAS- 3= Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.3 %) w/v

CAS- 4= Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.4 %) w/v

Thickness = ~ 0.10 mm



**Figure 1** Mechanical properties of the CAS composite membranes (a) tensile strength (b) elongation at break and (c) tear strength

**Table 2** Mechanical Properties of the (CASG) Composite Membranes Containing Various Concentrations of Glycerol

Membrane	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kNm <sup>-1</sup> )
CASG- 1	16.00	13.00	15.70
CASG- 2	20.50	18.00	42.50
CASG- 3	13.20	15.00	20.00
CASG- 4	9.20	32.00	14.40

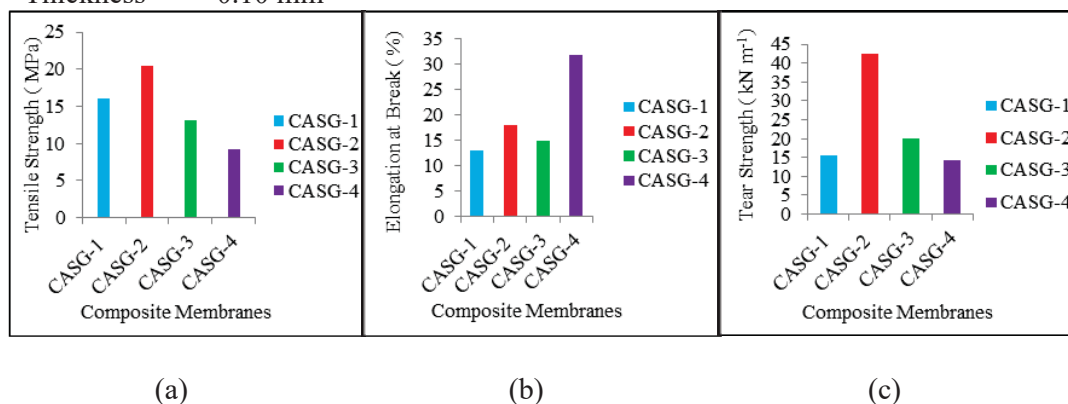
CASG- 1 = Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.3 %) +Glycerol (0.05 %) w/v

CASG- 2 = Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.3 %) +Glycerol (0.10 %) w/v

CASG- 3 = Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.3 %) +Glycerol (0.15 %) w/v

CASG- 4 = Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.3 %) +Glycerol (0.20 %) w/v

Thickness = ~ 0.10 mm



**Figure 2** Mechanical properties of the CASG composite membranes (a) tensile strength (b) elongation at break and (c) tear strength

**Table 3 Mechanical Properties of the (CASS) Composite Membranes Containing Various Concentrations of Sorbitol**

Membrane	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kNm <sup>-1</sup> )
CASS- 1	18.80	18.00	9.00
CASS- 2	30.00	17.00	16.00
CASS- 3	10.80	16.00	17.00
CASS- 4	26.30	25.00	7.00

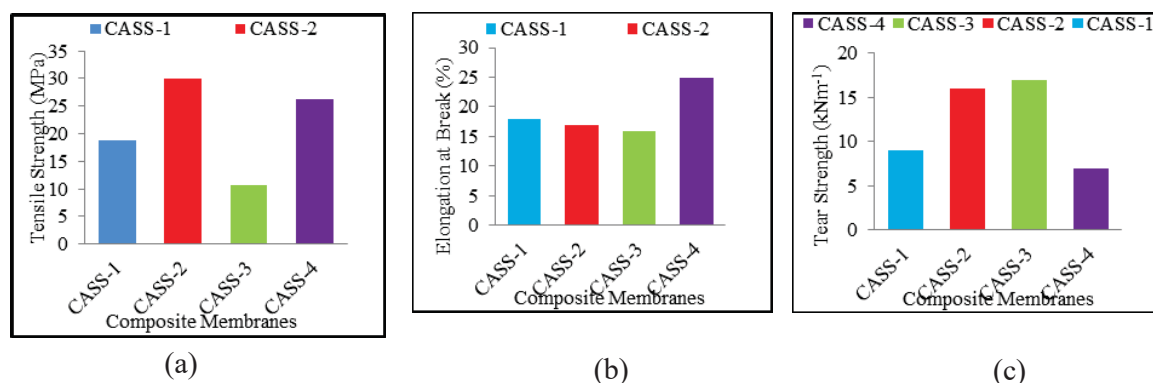
CASS- 1 = Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.3 %) + Sorbitol (0.05 %) w/v

CASS- 2 = Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.3 %) + Sorbitol (0.10 %) w/v

CASS- 3 = Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.3 %) + Sorbitol (0.15 %) w/v

CASS- 4 = Chitosan (1.5 %) +Alginate (3.0 %) +Starch (0.3 %) + Sorbitol (0.20 %) w/v

Thickness = ~ 0.10 mm

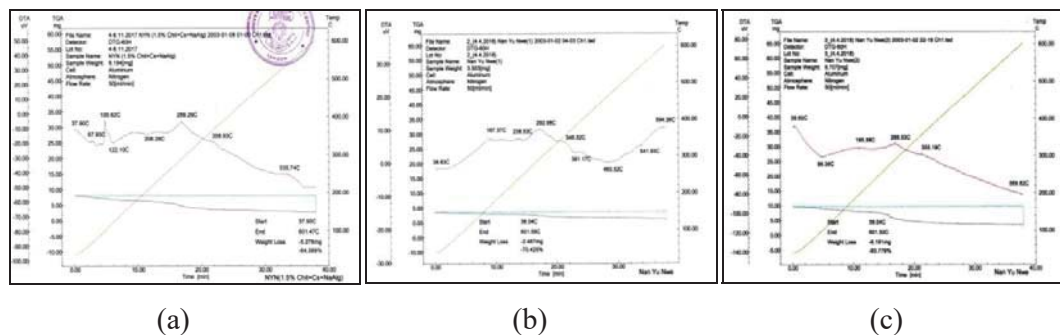


**Figure 3 Mechanical properties of the CASS composite membranes (a) tensile strength (b) elongation at break and (c) tear strength**

### Characterization of Selected CAS-3, CASG-2 and CASS-2 Composite Membranes

#### TG-DTA Analysis

The nature and remarks regarding the thermogram profiles are shown in Tables 4, 5 and 6. The thermograms of CAS-3, CASG-2 and CASS-2 composite membranes were presented in Figure 4. The TG-DTA thermograms showed marked features regarding the thermal stability of the membranes. The decomposition time (min) was presented on X-axis and TGA (mg) was presented on Y-axis. The temperature (°C) was also presented on Y-co-axis.



**Figure 4** TG-DTA thermogram of selected (a) CAS-3 (b) CASG-2 and (c) CASS-2 composite membranes

**Table 4** TG-DTA Thermal Analysis Data of Selected Chitosan-Alginate-Starch (CAS-3) Composite Membranes

Temperature range (°C)	Weight loss (%)	Peak's Temp: (°C)	Nature of Peak	TG Remark
40-130	18.31	100	exothermic	The first weight loss is due to the dehydration of absorbed water and moisture
		120	endothermic	
130-300	24.41	289	exothermic	The second weight loss is due to the removal of organic volatile materials
300-600	21.66	358	exothermic	The final weight loss is due to the degradation of biopolymer
		535	exothermic	

**Table 5** TG-DTA Thermal Analysis Data of Selected Chitosan-Alginate-Starch-Glycerol (CASG-2) Composite Membranes

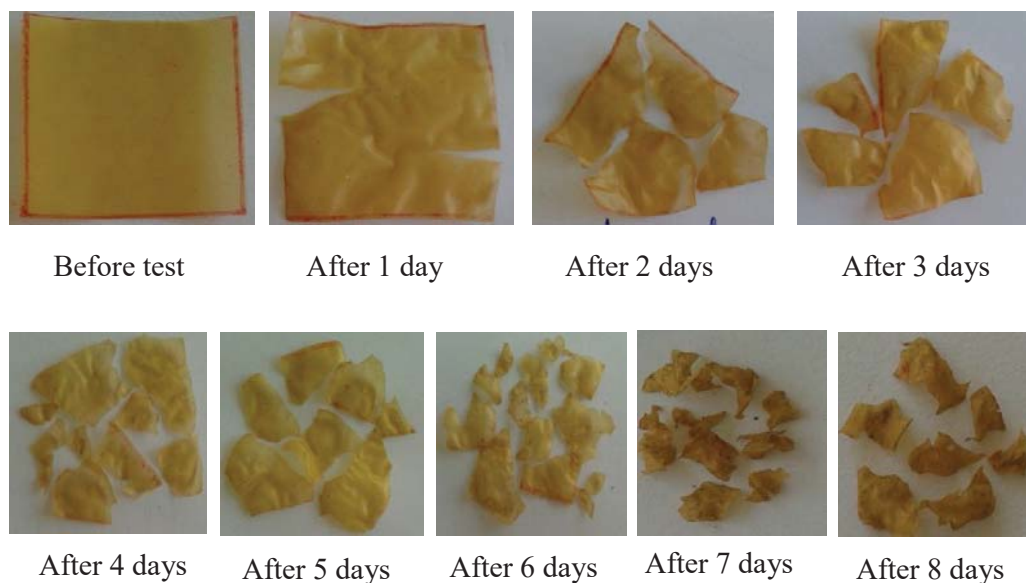
Temperature range (°C)	Weight loss (%)	Peak's Temp:(°C)	Nature of Peak	TG-Remarks
38-180	14.27	167	exothermic	The first weight loss is due to the loss of bound water from biopolymer
180-300	14.27	292	exothermic	The second weight loss is due to the combustion of volatile organic materials
300-600	41.89	346 460	exothermic endothermic	The final weight loss is due to the thermal decomposition of native chitosan, alginate, starch and glycerol by breaking their polymer network

**Table 6** TG-DTA Thermal Analysis Data of Selected Chitosan Alginate-Starch-Sorbitol (CASS-2) Composite Membranes

Temperature range (°C)	Weight loss(%)	Peak's Temp:(°C)	Nature of Peak	TG-Remarks
38-160	9.69	98	endothermic	The first weight loss is due to the loss of bound water from biopolymer
160-270	18.03	195	exothermic	The second weight loss is due to the combustion of volatile organic materials
270-600	36.06	288	exothermic	The final weight loss is due to the decomposition and degradation of polymer backbone

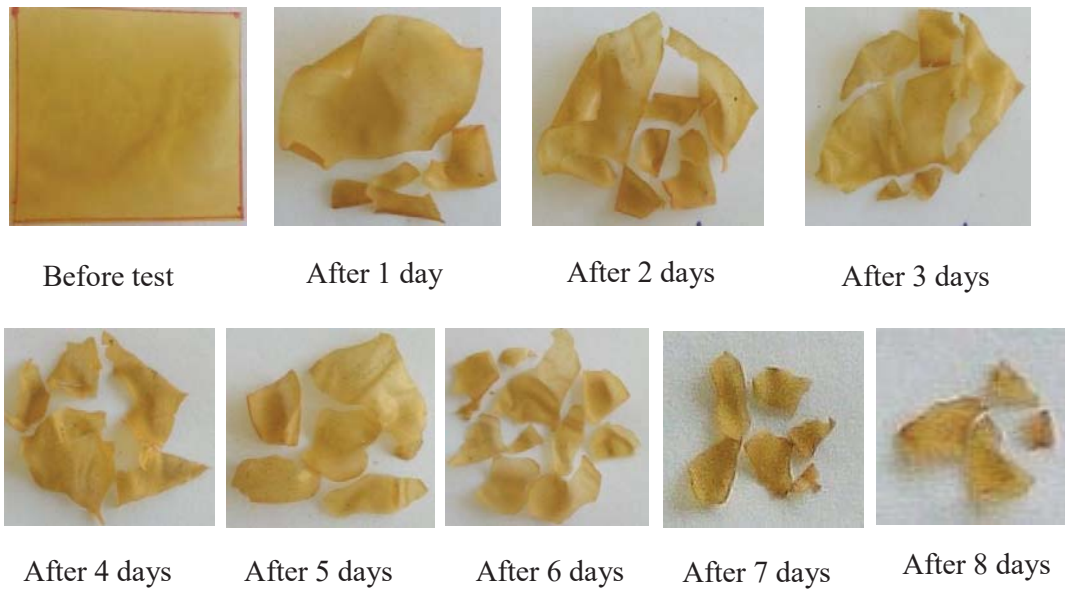
### On the Aspect of Biodegradation in Sandy Soil

In this work, biodegradation of prepared chitosan composite membranes were tested applying soil burial method. According to Figures 5-7 and Table 7, the membranes do not affect on the environment when they are buried in the soil which has got 38.75 % in moisture and 6.58 in pH value. 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 from waste disposal. The physical appearances of prepared chitosan composite membranes buried in the soil are shown in Figures 5-7 and Table 7. These figures clearly showed significant deformation of selected membranes.



**Figure 5** Physical appearance of chitosan-alginate-starch (CAS-3) composite membranes in sandy soil





**Figure 6** Physical appearance of chitosan-alginate-starch-glycerol (CASG-2) composite membranes in sandy soil



**Figure 7** Physical appearance of chitosan-alginate-starch-sorbitol (CASS-2) composite membranes in sandy soil

**Table 7**      **Degradation Weight Loss Percent of Selected (CAS-3, CASG-2 and CASS-2) Composite Membranes using Soil Burial Test in Sandy Soil**

Time (day)	Weight loss (%)		
	CAS-3	CASG-2	CASS-2
1	10.45	11.39	11.13
2	16.03	16.54	16.28
3	21.96	24.34	22.55
4	30.51	33.25	31.85
5	43.36	47.45	44.32
6	58.64	62.79	61.79
7	67.49	71.34	68.37
8	80.30	88.89	84.21

### Conclusion

In this study, polymer blended membranes consisting of chitosan, sodium alginate, starch and glycerol/ sorbitol solution were prepared. The various types of chitosan-alginate-starch composite membranes and modified chitosan-alginate-starch-glycerol/ sorbitol composite membranes were prepared by blending, casting and solvent evaporating technique under autoclaving conditions of 121 °C and 0.1 MPa in a time frame of 1 h. These prepared membranes have clear, smooth surface, flexible, highly transparent and light yellow colour. Based on the mechanical properties such as tensile strength, elongation at break (%) and tear strength, the optimum ratio was achieved by using 1.5 % (w/v) chitosan, 3.0 % (w/v) sodium alginate, 0.3 % (w/v) starch solution, 0.1 % (w/v) glycerol/ sorbitol. According to mechanical properties, CAS-3, CASG-2 and CASS-2 composite membranes were selected to be used for biodegradable applications. From TG-DTA analysis, three steps of weight loss percent showed in selected CAS-3, CASG-2 and CASS-2 composite membranes. The first weight loss showed due to dehydration of absorbed water and moisture. The second weight loss indicated that the removal of volatile organic materials. The third weight loss showed decomposition and degradation of polymer backbone. According to TG-DTA analysis, thermal stability of selected CAS-3 and CASS-2 composite membranes were found to be slightly more than CASG-2 composite membrane. Biodegradabilities of CAS-3, CASG-2 and CASS-2 composite membranes were studied by soil burial method in sandy soil. Biodegradation was determined by soil burial test examining the weight loss and morphology changes. The physical appearances of selected chitosan composite membranes exhibited significant deformation in nature.

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