INVESTIGATION ON OXYGEN PERMEABILITY AND SURFACE PROPERTIES OF AGAR FILMS

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Abstract

In this work, agar (AG) films have been prepared using the cast method technique. Surface properties such as contact angle (CA) and morphology of the films were carried out. The water contact angle on the surface of agar film was recorded to be $74.91^{o}\pm0.35$ indicating good hydrophilicity of the surface, which was confirmed by the scanning electron microscope (SEM) image of the AG film. The contact angle was also studied with the variation of time. After making the initial contact on the substrate, the water contact angle on the AG film was found to decrease gradually with time. Studying the oxygen permeability of the agar film showed that the film had an oxygen permeability of about 187 barer.

Keywords: permeability, properties, agar, film

Introduction

Agar, a gel forming polysaccharide, is a hydrophilic colloid extracted from the family of seaweeds (Rhodophycae) having a common backbone structure: 1,4-linked- 3,6 -anhydro-α-L-galactopyranose (Figure 1) (Araki et al, 1967). Agar is insoluble in cold water and slightly soluble in ethanolamine. However, it is soluble in hot water in the dried state (Phan et al, 2005). One of the most important properties of agar is its ability to form reversible gels even at low concentration simply by cooling its hot aqueous solutions. This is due to the formation of hydrogen bonds (Stephen et al, 1995; Glicksman, 1979; Armisen & Galatas, 2000). This has given agar a wide use in a variety of industries including food industry products such as processed cheese, ice cream, bread and soft candy (Armisen, 1995; Freile-Pelegrín et al, 2007).

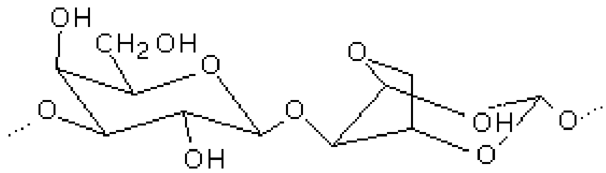

Figure 1: Original structure of agar repeat unit.

In this study, we report on an investigation of the oxygen permeability, contact angle and morphology of agar films with a view to further explore the properties of the agar thin film and films of its mixture with other selected polymers.

Experimental part

Materials

Agar was purchased from Sigma-Aldrich *and its* average *molecular weight* was 1.3 $\times 10^4$ g mol^{-1}. All solutions were prepared using ultra pure water (Maxima Ultra Pure Water, Elga-Prima Corp, UK) with a resistivity greater than 18MΩ/cm.

Film Preparation

Agar powder was dissolved in hot double-distilled water and stirred at temperature of 90^{o}C. After stirring for about 2 hours, the optically clear solution was obtained. 10 mL of the solution was then poured into polystyrene petri dish followed by drying at 60^{o}C for 48 h. The resultant films were peeled off gently and kept under evacuated desiccator over fresh silica gel until use. All obtained films were transparent and free of air bubbles. The flow diagram for preparation of agar films is summarized in Figure 2.

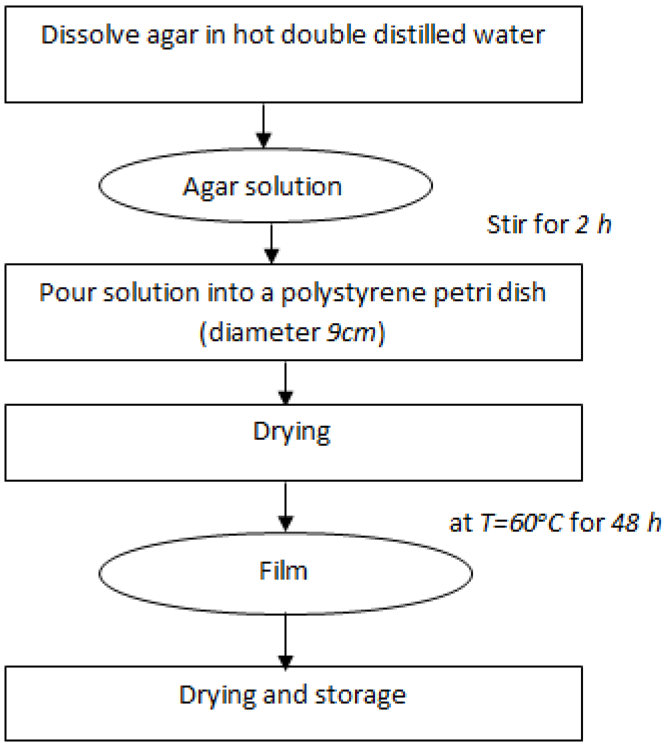

Figure 2: Flow diagram for preparation of agar films

Film Thickness

The film thickness was determined using a digital micrometer (Mitutoyo, Japan) with resolution of 0.001mm. Several thickness measurements were taken at several points of the film and then, the average was calculated. The thicknesses of the films were around 15µm.

FESEM Measurements

Surface morphology was investigated by a FEI Quanta 200F field emission scanning electron microscope (FESEM) (FEI, USA) controlled by a 32 bit computer system using Microsoft Windows 2000 as an operating system.

Contact angle measurements

The static water contact angles of the films were measured at room temperature by the drop method using an optical *contact angle* meter *CAM 200* (*KSV* Instruments Ltd, *Helsinki*, *Finland*) to examine the surface wettability of the films. The substrates used for the experiments were glass *microscope slides* (25.4 × 76.2 mm, 1-1.2 mm thick). Each slide was cleaned before use by soaking in ethanol overnight. 7 µ L of distilled water was carefully injected on the film surface before measuring. The contact angles were measured on both sides of the drop and averaged. The reported contact angle was the mean value of at least 10 measurements.

Gas Permeation Test

Permeation test was conducted for the agar films using a variable volume apparatus attached to a local design soap bubble flow meter as presented in Figure 3. The membrane films were cut into a rounded shape with a diameter of 5 cm. Afterwards, it was mounted between the upper and lower parts of the cell, followed by clamping and sealing tightly with a rubber O-ring. The measurement was conducted at room temperature over a pressure of 1.0 and 3.0 bars. Oxygen gas at specific pressure was fed into the system. After the gas flow in the permeate side reached steady state, the volumetric gas permeation rates were recorded.

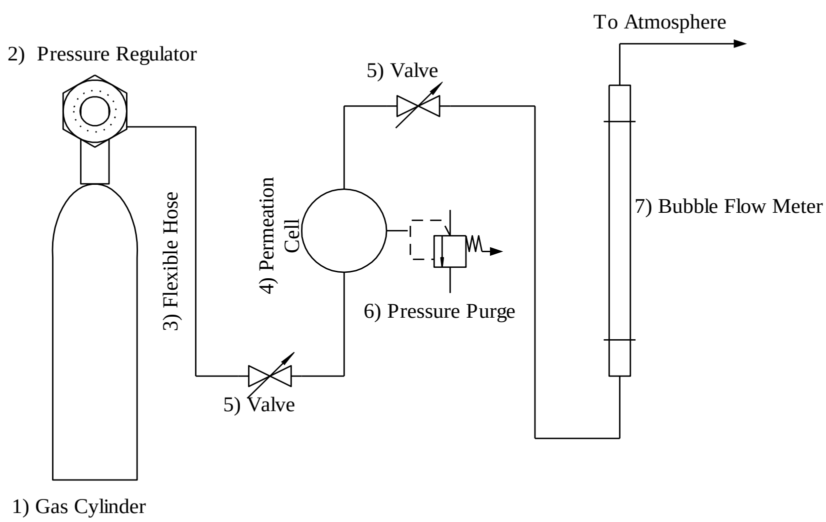

Figure 3: Schematic diagram of soap bubble flow meter used in this work

Pressure normalized fluxes, (P/L)*i* of O_2 were determined from bubble flow meter measurements by:

$$\left(\frac{P}{L}\right)_i = \frac{Q_i}{(\Delta P)(A)}$$

where Q_i is volumetric flow rate of gas *i* at standard temperature and pressure, ΔP is the trans membrane pressure drop and *A* is the membrane surface area.

Pressure – normalized gas fluxes are often reported in gas permeation units, GPU, where:

$$GPU = 1x10^{-6}\ cm^3\ (STP)/cm^2 scmHg$$

Results and discussion

Oxygen permeability of agar hydrogel membrane

Oxygen permeability of agar was successfully measured in this work to be 187 barrer. The data and detailed calculations for oxygen permeability are shown in Table 1.

Table 1: Pure O_2 gas permeation results for pure agar.

	Trial No.	T (s)	V (cm^3)	Q (cm^3/s)	A(cm^2)	L (cm)	□p (cmHg)	P ($cm^3.cm/s.cm^2.$ cmHg)	P (barrers)
1 bar	1	52	1.0	0.019231	13.26	0.0001	75	1.93371E-09	193.3712
	2	55	1.0	0.018182	13.26	0.0001	75	1.82824E-09	182.8237
	3	54	1.0	0.018519	13.26	0.0001	75	1.86209E-09	186.2093
	Average	**53.67**		**0.018644**	**13.26**	**0.0001**	**75**	**1.87468E-09**	**187.4681**
3 bar	1	17	1.0	0.058824	13.26	0.0001	225	1.97163E-09	197.1628
	2	20	1.0	0.05	13.26	0.0001	225	1.67588E-09	167.5884
	3	17	1.0	0.058824	13.26	0.0001	225	1.97163E-09	197.1628
	Average	**18.00**	**1**	**0.055882**	**13.26**	**0.0001**	**225**	**1.87305E-09**	**187.3047**

Surface hydrophobicity and wettability

The contact angle of the water droplet deposited into the surface of films is commonly used to describe their *hydrophobicity*/hydrophilicity, which is generally used to estimate the resistance of the film against liquid water (Phan et al, 2009; Rhim et al, 2006). Generally, the more hydrophilic a material is, the lower the CA value it has (Rhim et al, 2006). In this work, a contact angle of $74.91^o \pm 0.35$ was observed for the AG film, which is less than 90^o, indicating good hydrophilicity of the surface. This was in agreement with the SEM image of the AG film, which showed a quite rough surface (Figure 4). The value of contact angle of AG film recorded in this work is lower than the one reported by Phan et al (2009) for agar based film (92^o)**.** This is acceptable since the source of agar and the thickness of this kind of films could have an effect on the contact angle measurement. The mapping and chemical analysis are shown in Figure 5 and summarized in Table 2.

Generally, the water droplet spreads out faster on soluble films surface than on surface of insoluble and swollen films. Since AG films are swollen, we expect a gradual spreading of the water droplet on its surface with time. Figure 6 shows the variation in the water contact angle with time for the AG film. The contact angle of the AG film decreases gradually after making the initial contact on the substrate due to the hydrophilic nature of AG. The change in contact angle with time could be due to evaporation and surface oxidation:dissolution (Raichur et al, 2000).

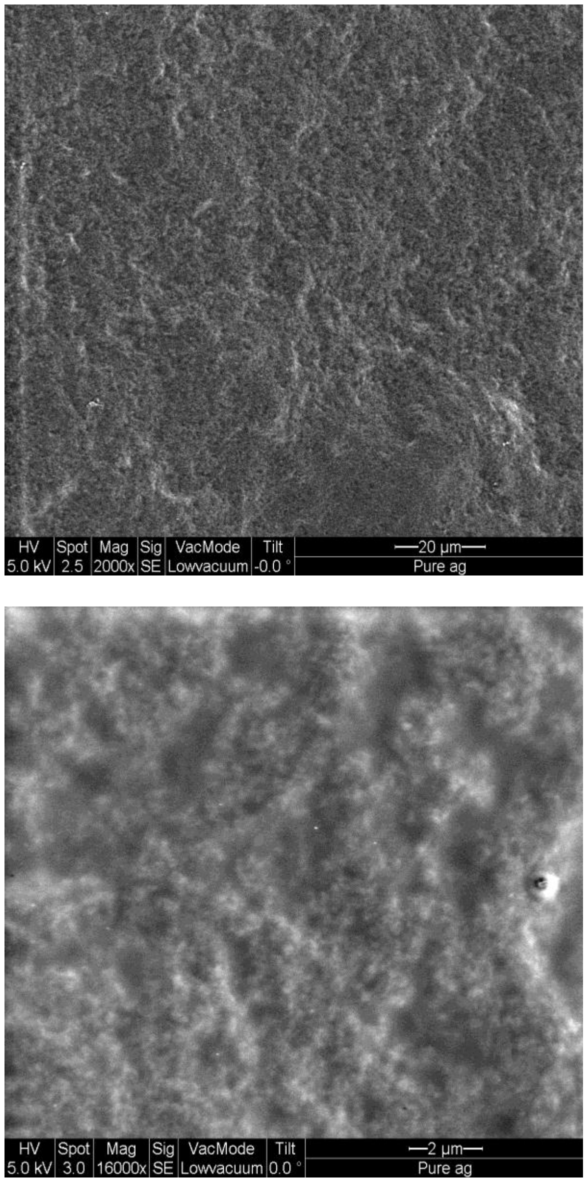

Figure 4: SEM micrographs of agar film (El-hefian et al, 2012).

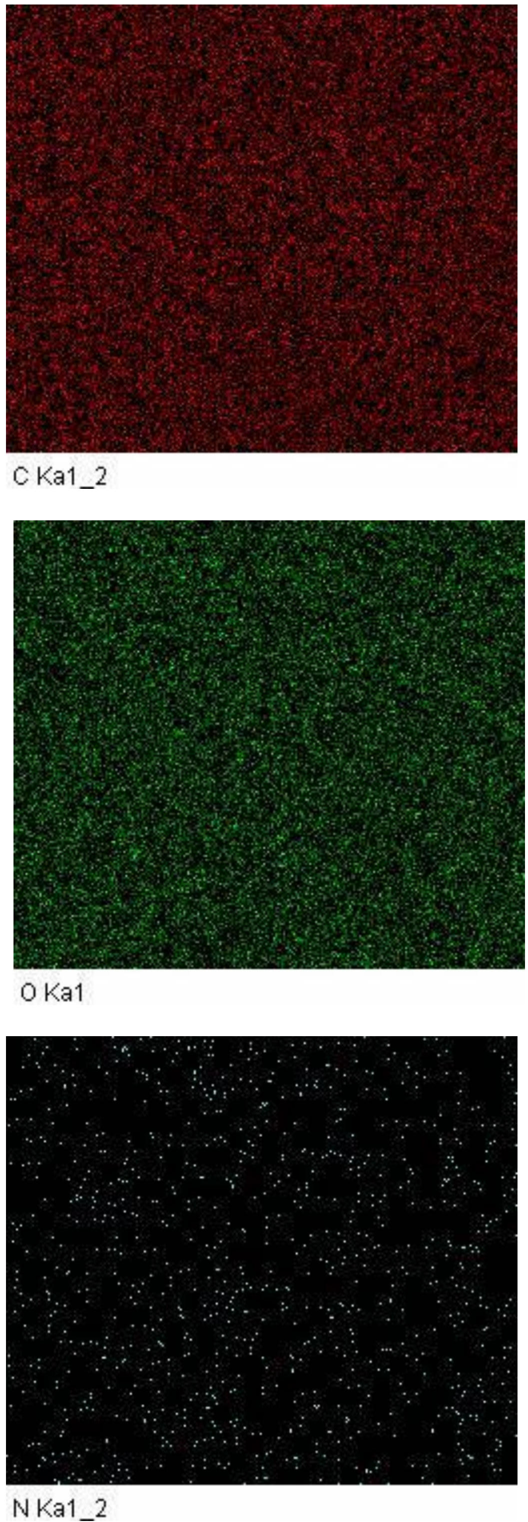

Figure 5: Mapping analysis of agar film.

Table 2: EDX (Energy Dispersive X-ray) analysis of agar film.

Element	Weight%	Atomic%
C	43.02	49.57
N	10.34	10.22
O	46.13	39.91
Na	0.51	0.31
Totals	100.00	

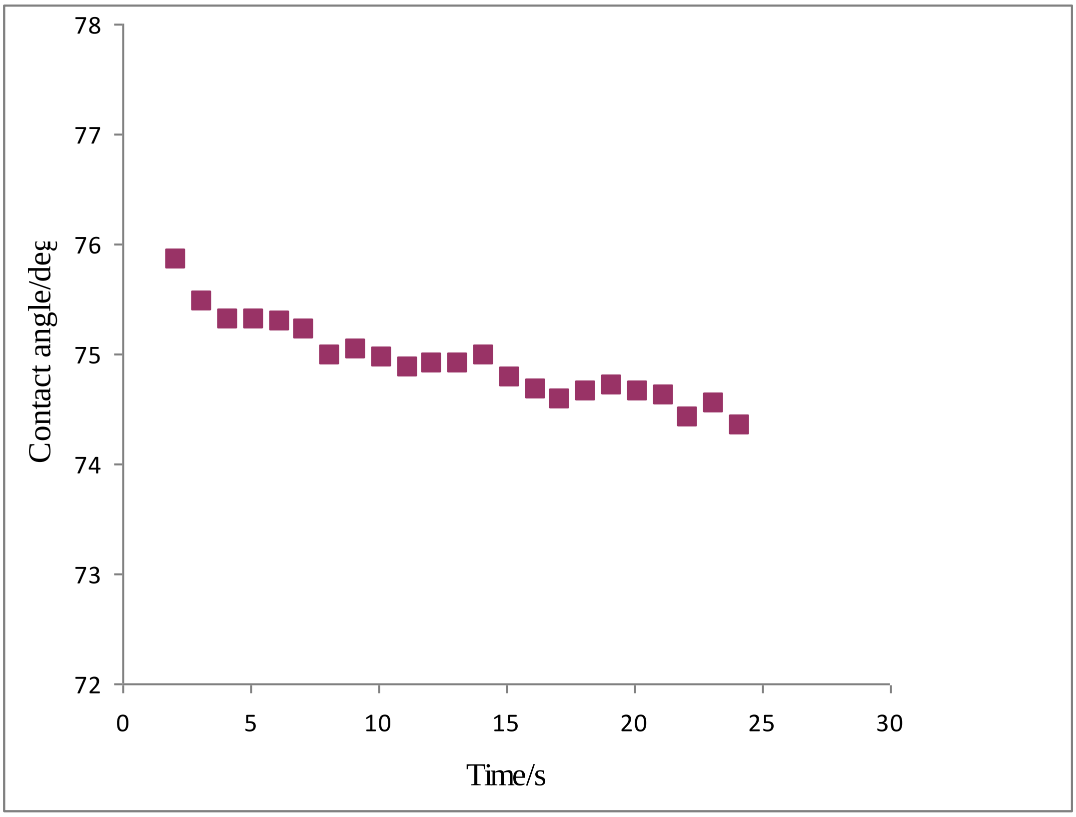

Figure 6: Variation of water contact angle on agar film with time.

Conclusion

This work has shown good hydrophilicity of agar films as indicated by surface properties i.e., contact angle and morphology. Water contact angle on the surface of agar film was found to be 74.91^{o}± 0.35. The contact angle was also studied as a function of time. After making the initial contact on the substrate, the water contact angle on the AG film decreased gradually with time. On the other hand, oxygen permeability of agar film was determined to be 187 barrer using the bubble soup flow meter method.

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