THE INFLUENCE OF THE PLASTICIZER ON THE QUALITY OF EDIBLE AGAR-BASED FILMS

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Abstract: This study aims to investigate the influence of glycerol on agar-based films. It has identified the optimal plasticizer concentration in order to obtain a film with superior characteristics unlike the one obtained 100% from agar. The film with the best properties was obtained from 1.5 g agar and 1 g glycerol: flexibility, smoothness, transparency, homogenous structure without any pores or cracks. Although having lower solubility than the film made entirely from agar, it is not suitable for packaging liquids orhigh humidity products; in this case, films will be enhanced with lipid compounds, which will increase the degree of hydrophobicity of the material.

Key words: edible film, packaging, agar, glycerol.

Introduction

Nowadays, there is a continuing concern regarding the production of biodegradable materials that can successfully replace conventional plastic packaging. Biopolymers are made from renewable resources, mostly polysaccharides and vegetable or animal proteins, but can also be obtained through chemical synthesis of natural monomers (lactic acid). [1] They are biodegradable, can be easily processed, and have suitable properties for bioplastic production. [2]

Agar is a polysaccharide extracted from *Rhodophytaceae* (*Gelidium* or *Gracilaria* species) [3], [4]. Used for the production of packaging materials, agar has good mechanical properties, but high solubility [5]; it is used in combination with other biopolymers, such as starch, milk or soy proteins, for improving the mechanical and barrier properties. [6], [7] The most important feature is its ability to form strong gels in extremely low concentrations (0.04%) [8], being used as a gelling agent in food or pharmaceuticals industry, cosmetics, biotechnology, and medicine. [9] Due to the thermoplastic, biocompatibility, and biodegradability character, it can be used as a substitute for conventional plastic packages. [9], [10]

The films used for food packaging can be consumed simultaneously with the product it protects; even though it should not have any taste, smell, colour so as not to alter the product properties, the food industry has created films with added flavour, colour, smell compounds, antioxidants and antimicrobial agents [11-15] in order to obtain top grade products. In order to improve the agar based films properties, glycerol is one of the most widely used plasticizer. [16]

The main objective of this study has been to determinate the optimal concentration of glycerol necessary to obtain agar-based edible films that could successfully replace conventional packaging in food industry.

Materials and methods

Materials

The agar and glycerol used for this study were purchased from Sigma Aldrich Inc.

Preparation of agar and glycerol films

The films were prepared according to the method described by Rhim, J.W. [17], with some modifications. In order to obtain plasticized films, the agar was replaced by glycerol in a proportion of 20, 30, 40, 50, and 60% respectively. The obtained solution was stirred for 30 minutes and 300 rpm, and temperature of 95ºC, cast on a silicone surface and maintained at temperature of 20ºC until the film was bone-dried.

Table 1. Preparation scheme of agar and glycerol solutions

Assay	**m_{Agar}, (g)**	**$m_{Glycerol}$, (g)**	**$V_{distilled\ water}$, (ml)**
P_1	2.5	0	200
P_2	2	0.5	
P_3	1.75	0.75	
P_4	1.5	1	
P_5	1.25	1.25	
P_6	1	1.5	

Properties and characterization of obtained films

The physical properties such as homogeneity, colour, odour, taste, transparency, and flexibility were evaluated.

Film thickness

The thickness of films was determined by using an electronic micrometre with a precision to 0.01mm. The measurement was performed in at least five randomly chosen locations and their average was noted.

Film microstructure

Film microstructure was observed by scanning electron microscopy (SEM, Motic Microscopes). The obtained films were observed in initial form and after water immersion; matrix appearance and the presence of pores and cracks were observed.

Surface colour of films

It was performed using Chroma-Meter CR-400 (Konica Minolta) colorimeter. A white standard colour plate (L= 92.61, a= -0.66, b=4.15) was used as background for colour measurements. Hunter colour (L, a, b) values were averaged from three readings of each sample. The total colour difference (ΔE) was calculated as follows:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{0.5} \quad (1)$$

where ΔL, Δa, Δb are differences between each colour values of standard colour plate and film, respectively.

Swelling ratio

It was determined using the following formula:

$$CH (\%) = (W_s – W_u)/ W_u \times 100 \quad (2)$$

where W_s, W_u are the weights of swollen and unswollen films, respectively.

For the measurement of swelling ratio, films were cut into small pieces and weighed, then immersed in distilled water for 30-1230 seconds at 20ºC. The films were taken from the water and the excess water was removed and reweight.

Results and discussion

Film characterization

The obtained films were homogenous, thin, flexible and transparent. In terms of colour characteristics, they showed a slightly yellowish colour, whose intensity increased with the increasing mass of agar; they had no taste or smell. Except the film made entirely from agar, with pores in its structure, the other films, made with agar and glycerol, were easily removed from the silicone foil, with no pores or cracks. The film obtained from agar and distilled water (P_1) had a yellowish hue, was rigid, slightly brittle, relatively opaque, with uniform distribution of the hydrocolloid. It was dried after 40-hour maintenance at ambient temperature. The drying time of P_2 was 38 hours; in contrast to the first sample, it presented improved properties. The third film was bland, relatively uniform, transparent, soft, smooth, thin, dried in 69 hours. P_4 has the same appearance, yet thinner, although the drying time was the same. The sample obtained from the same quantity of agar and glycerol was very thin, soft, transparent, with relatively uniform distribution of agar, completely dry after 75 hours. The film made from the highest content of glycerol was extremely thin, with inequable distribution of agar and yellowish coloration in some areas, very soft, dry after 4 days of soaking at 20ºC.

Film thickness

The thickness of the films varied from 0.04 to 0.07 mm (table 1).The thickness had a great influence on appearance, thinner films being colourless, transparent, fine, and dried faster, meanwhile films with 0.06-0.07 thickness were opaque, inflexible, brittle, stained dark yellow.

Table 1. Thickness and apparent surface colour of films

	Thickness (mm)	**Colour**			
		L	**a**	**b**	**ΔE**
P_1	0.07	85.22	-0.37	12.69	51.29
P_2	0.065	87.86	-0.61	11.40	53.95
P_3	0.06	88.61	-0.68	10.60	54.74
P_4	0.055	88.16	-0.68	10.48	54.32
P_5	0.05	89.32	-0.80	9.63	55.52
P_6	0.04	89.34	-0.81	9.07	55.60

Film microstructure

The images obtained by electronic digital microscope reveal the presence of small pores, but no cracks, when the film is entirely made from agar (as can be seen in

Fig. I, P1a). The same behaviour of non-plasticized agar-based films was highlighted by Phan The et. al. [18].

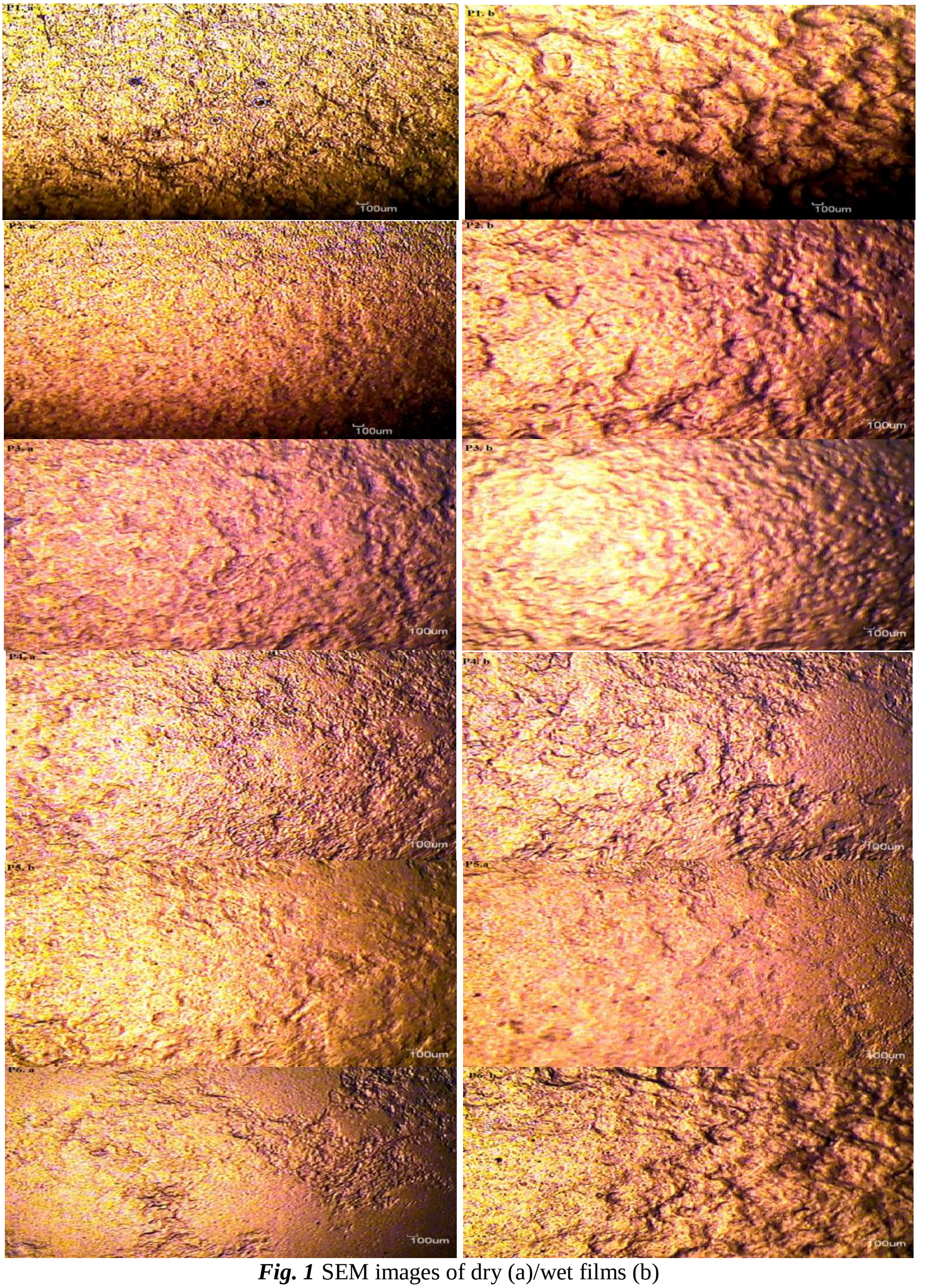

Fig. 1 SEM images of dry (a)/wet films (b)

The obtained images highlight the swelling capacity of agar granules (aspect especially observed in case of P_6 sample, where the dispersion degree can be see

Surface colour of films

The agar-based film (P_1) showed a slightly yellowish colour, with low brightness, as evidenced from the results shown in table 1. As the agar content was replaced by glycerol, films became more transparent, flexible, fine, smooth, relatively colourless. The fact that they have not changed the colour of the food they protect is extremely important for their use in food packaging industry.

Swelling ratio

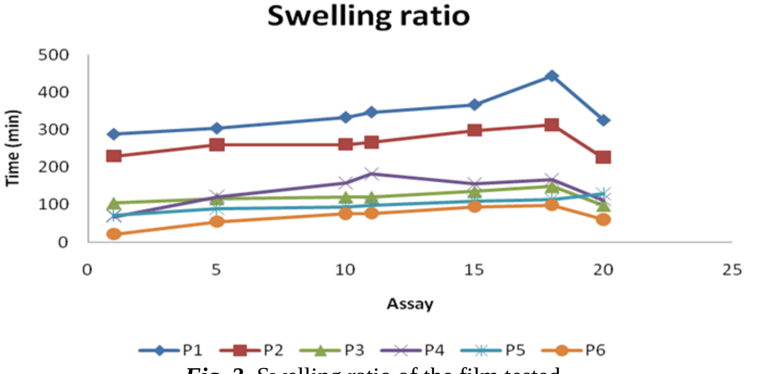

Fig. 2. Swelling ratio of the film tested

There is a tendency to increase the swelling ratio according to the increased immersion time. P_1 showed an inflation granules trend, aspect observed in SEM images. With the addition of glycerol, swelling ratio values were reduced as the film matrix has become compact and the water molecules were positioned in a smaller place than the films without added plasticizer. The swelling ratio of six samples was turn out to be high, amounting to 443.86% after 18 minutes of immersion of the film obtained without plasticizer addition. Regarding the breakage trend of wet films, P_4 distorted after 17 minutes of water immersion, meanwhile P_5 and P_6 were broken after 15 minutes. The film made entirelyfrom agar strained after 8 minutes, highlighting, once again, the need of plasticizer for packaging development.

Conclusions

This study aimed to highlight the optimal plasticizer concentration in order to obtain agar-based edible films used for food packaging industry. The results indicate an ideal recipe at sample obtained from 60% agar and 40% glycerol; this proportion of plasticizer led to homogenous, transparent, colourless, odourless, without pores or cracks films. Although samples with glycerol showed lower solubility than those obtained only from agar, these cannot be used for liquids or high humidity products. If we take into account the addition of lipids or other hydrocolloids into composition, this aspect can be improved, making them suitable for food industry.

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