

Study on the effects of plasticiser types and contents on physicochemical properties of HPMC/Shellac composite films

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Received 24 September 2021; revised 20 November 2021; accepted 29 November 2021

Abstract:

The objective of this work was to study the effects of different plasticisers [glycerol (G), propylene glycol (PG), polyethylene glycol 400 (PEG 400)] at different contents (10-30% compared to hydroxypropyl methylcellulose (HPMC)) on the properties of HPMC/shellac composite films. Sensory, mechanical properties, and surface morphology were used to evaluate changes in the composite films by adding different plasticisers. The results showed that with the addition of plasticisers, the films became more transparent and flexible. As the plasticiser content increased, the tensile strength and elastic modulus of the films decreased. At a plasticiser content of 20%, the water vapor permeability (WVP) of the composite films reached its minimum value. The SEM images showed that the HPMC/shellac composite film containing 20% G had the smoothest surface, and the components of this film were uniformly distributed.

Keywords: composite film, hydroxypropyl methylcellulose, plasticiser, shellac.

Classification number: 2.2

1. Introduction

In recent years, our country's agricultural production has made enormous progress but lacks sustainability. Given that vegetables and fruits have water contents around 80-90% of their total weight, they are very perishable [1], which leads to high post-harvest losses of agricultural products. Indeed, more than 25% of fruits and more than 30% of vegetables are lost due to lack of post-harvest technology. Therefore, the technology of preserving vegetables and fruits in order to prolong storage times while maintaining their commercial value has been the focus of research and development by scientists. Among the methods of preserving fruits and vegetables being researched and used today, biopolymers are very interesting not only because they have outstanding advantages over petroleum-based polymer films, but because of their biodegradable and environmentally-friendly properties. A biopolymer film is a thin material layer used to coat the surface of vegetables/fruits or to replace the natural protective wax and provide a moisture and oxygen barrier. This film is placed directly on the

fruit surface by dipping, spraying, or sweeping to create a modified atmosphere (MA). The semi-permeable film formed on the surface of the vegetables/fruits restricts their respiration and controls moisture loss, as well as limits the release of active compounds such as antioxidants, flavours, or antibacterial agents [2]. Such films have been used to maintain quality and prolong the shelf life of some fresh fruits such as citrus fruits (oranges, lemons, and tangerines), apples, and cucumbers. They have advantages such as retention of pigments, sugars, acids, and aromas, as well as reduction of mass loss, maintenance of quality during transportation and storage, improved consumer appeal, and prolonging the shelf life [3]. Coating materials are commonly used from materials of biological origin and certified as safe for humans such as proteins, polysaccharides, and lipids.

HPMC is one of the matrix materials used directly on the surface of fruits and vegetables because it has good film forming ability, is odourless, tasteless, has good air permeability, and retains the product scent. However, the disadvantage of HPMC is that it is hydrophilic, so recent

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research directions aim to combine natural and synthetic waxes such as beeswax, shellac, paraffin wax, etc. into film formulae to improve water vapor barrier properties as well as combine the beneficial properties of both film-forming materials. In addition, plasticisers are also added to increase the flexibility of the film [4-6], the most commonly used plasticisers are polyols such as sorbitol, G, PG, and PEG 400. Therefore, this paper focuses on evaluating the influence of different plasticisers on the physico-chemical properties of HPMC/shellac composite films.

2. Materials and methods

2.1. Materials

HPMC E15 resin was produced by Zhejiang Joinway Pharmaceutical Co. Ltd., (China) and dewaxed shellac was supplied by Raj Kumar Shellac Industries (India), both of which are food grade. Other chemicals: G, PG, PEG 400), lauric acid, absolute ethanol are all pure chemicals made in China and used directly without refining.

2.2. Methods

2.2.1. Preparation of the HPMC/shellac composites

- To prepare the colloidal solution of HPMC, 5 g HPMC was dispersed in 80 ml of distilled water at 80°C and stirred at rate of 200 rpm until completely dissolved. Then the solution was lowered to 40-50°C and the plasticisers (G, PG, PEG 400) were added with weights of 0.5-1.5 g (content of 10-30% as compared to HPMC) and stirring was continued at 200 rpm for 120 min.

- To prepare the emulsification of the shellac, 0.1 g shellac and 0.01 g lauric acid were put into a beaker containing 20 ml of absolute ethanol, and the mixture was stirred at 200 rpm for 120 min and then filtered through Whatman filter paper No.5.

- The shellac emulsion was slowly poured into the HPMC solution, and the mixture was stirred at 300 rpm for 180 min to obtain a composite film forming solution.

To evaluate the properties of the HPMC/shellac composite films, 6 ml of the film-forming solution was put into a petri dish (diameter of 100 mm) and then placed in an oven and dried at 40°C until dry. After drying, the film was removed from the petri dish and stored in a desiccator for at least 24 h before measurements and testing. The symbols of the film samples are summarised in Table 1.

Table 1. The symbols of film samples.

Sample symbols	Plasticizer	Content of plasticiser as compared with HPMC (%)
0.5 G	Glycerol	10
1 G		20
2 G		30
0.5 PG	Propylene glycol	10
1 PG		20
2 PG		30
0.5 PEG	Polyethylene glycol	10
1 PEG		20
2 PEG		30

2.2.2. Characterisation

The surface morphology and fracture surface morphology of the HPMC/shellac composite films were investigated by using a JEOL SM-6510 LV device (Japan). The surface of the sample was coated with a thin gold layer by vacuum evaporation to increase contrast. The mechanical properties were measured on a BP-1068 instrument according to ASTM D882 with a tensile speed of 10 mm/min. WVP was determined according to ASTM E96.

3. Results and discussion

3.1. Sensory evaluation of films

Sensory evaluation is a simple, effective tool that gives information about the appearance, colour, and durability, which could be related to other properties such as mechanical properties, surface morphology and WVP to select suitable film features. Photographs of composite films using different plasticisers at different concentrations are shown in Fig. 1.

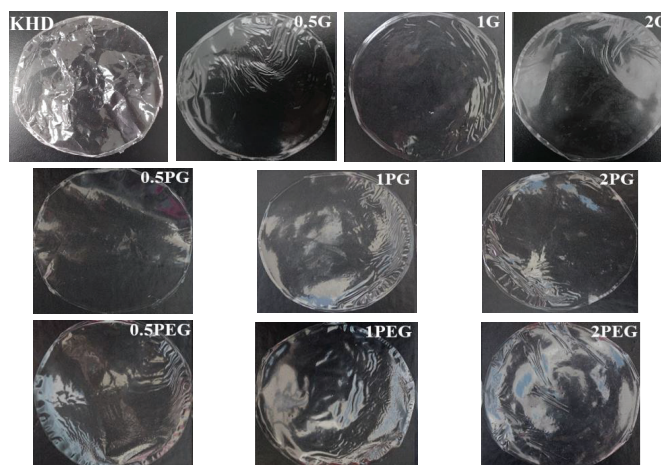


Fig. 1. Photograph of the HPMC/shellac composite films without plasticiser (KHD) and with various plasticisers.

The results showed that in the absence of plasticisers the films were brittle, hard, fragile, and difficult to peel. This was because both the main film-forming materials were HPMC and shellac, which had -OH groups forming intramolecular and intermolecular H bonds. When adding plasticisers to the film, the film became more transparent and glossier, and the surface of film was smoother.

When using G as a plasticiser, the film with 10% G was still brittle and the film with 20% G was flexible and unbroken, while the film with 30% content was too flexible, difficult to form, and viscous. This could be because with the same film forming formulation, 10% G, was not enough to fully plasticize HPMC and at 30% content, the excess G molecules had migrated to the film surface thus forming a sticky and viscous film [7, 8].

Just like G, the film with 10% PG was not flexible and broke easily when peeled off. The films with 20% PG was flexible and did not break when peeled off, while the film with 30% PG was too flexible and presented oil scum on the surface of the film after drying. However, the films containing PG plasticiser were often weak because of the weak polarization of PG [9].

Particularly, the surface of the films containing the PEG 400 plasticiser with all three concentrations of 10, 20 and 30% was smooth and did not break during the peeling process. However, the film with 10% PEG 400 was still brittle, and the film with 30% PEG 400 gave a very flexible film, presented oil scum on the surface of the film, and they had less elasticity than the 1 PEG film. With 20% content, the film was glossy, beautiful, and had good tensile strength and elongation at break [10]. Therefore, it could be seen that PEG, a plasticiser with a small molecular mass, easily interacted with the polymer chains and increased the flexibility of the films.

Thus, when using plasticisers, the activity and flexibility of the polymer chains were improved due to interaction between the polymer chains and the plasticiser, which increased the molecular mobility. However, with the same plasticiser content of 20%, the film containing the G plasticiser was more elastic and flexible.

3.2. Surface morphology of films

Since plasticisers contain polar -OH groups, it was possible to strengthen interactions between surface of

polymer and water molecules by reducing the polymer matrix density and increasing the degree of polymer chain flexibility. Surface and fracture surface SEM images of HPMC/shellac films are shown in Figs. 2-4.

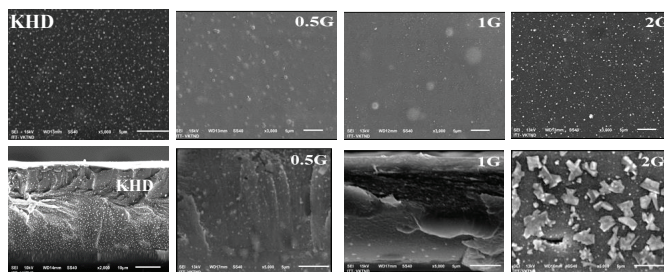


Fig. 2. SEM images of surface (top) and fracture surface (bottom) of the films using G plasticiser.

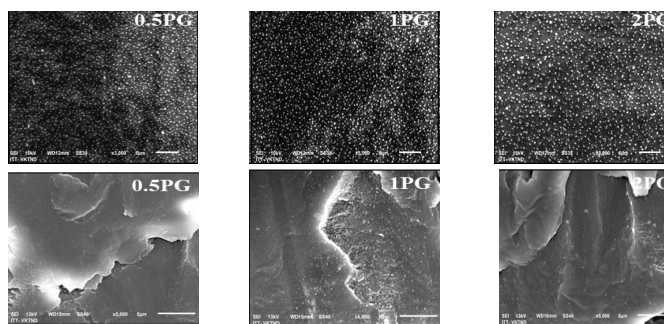


Fig. 3. SEM images of surface (top) and fracture surface (bottom) of the films using PG plasticiser.

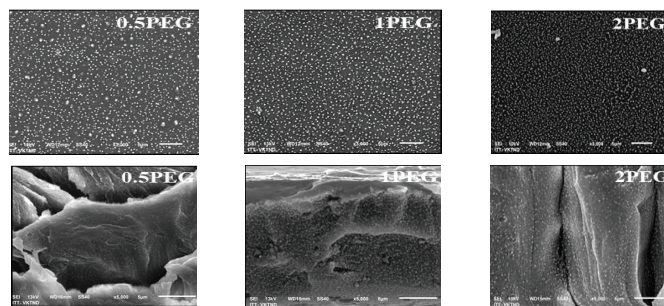


Fig. 4. SEM images of surface (top) and fracture surface (bottom) of the films using PEG plasticiser.

Observing surface and fracture surface SEM images of HPMC/shellac composite films, it was found that in the absence of plasticisers, the film surface was rough and defects appeared on the film surface. At the fracture surface, there were discontinuities in the polymer matrix structure and capillaries and pores appeared. When using plasticisers, the components of the film dispersed into each other more evenly. This might be because plasticisers acted as spacers between polymer chains thereby reducing the intermolecular forces and increasing the flexibility of the polymer chains [11]. In

all three plasticisers, it was found that the components in the film were most evenly distributed with 20% content. This proved that 10% plasticiser content was not sufficient enough to plasticize other components in the film. Meanwhile, at 30% content, the plasticiser carries other components to the surface and causes the appearance of particles. It was also found that increasing the plasticiser concentration increased the diffusion rate of the components in the film and when the diffusion rate was high, it led to the migration of plasticisers out of the polymer matrix [9].

Comparisons of surface SEM images of the films using different plasticisers showed that the films with 20% G plasticiser had the smoothest surface, small particles, and plasticized film components.

3.3. The mechanical properties of the composite films

The mechanical properties of the HPMC/shellac composite films with different plasticisers are summarised in Table 2. The results showed that when the plasticiser content increased, the tensile strength and elastic modulus of the films decreased with all three plasticisers. When the plasticiser content was increased from 10 to 30%, the tensile strength of films decreased from 25.23 to 16.49 MPa for films containing G, from 29.45 to 21.12 MPa for films containing PG, and from 32.54 to 15.83 MPa for films containing PEG 400. Meanwhile, the elongation at break of the films increased with increasing content of plasticisers. This could be explained that the addition of plasticisers made polymer chains more flexible by replacing polymer-polymer interactions with polymer-plasticiser interactions [5].

Table 2. The mechanical properties of films with different plasticisers.

Samples	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus ($\times 10^{-2}$ MPa)
0.5 G	25.23	11.89	10.92
1 G	17.02	28.41	2.93
2 G	16.49	32.62	1.74
0.5 PG	29.45	3.91	17.37
1 PG	26.85	7.70	15.37
2 PG	21.12	15.47	12.08
0.5 PEG	32.54	17.29	14.37
1 PEG	24.45	26.56	8.32
2 PEG	15.83	32.00	1.60

Comparing the mechanical properties of the films when using different plasticisers, it could be seen that the mechanical properties of the HPMC/shellac composite

films did not change much by using the PG plasticiser. This could be because PG has a lower polarity than G and PEG 400, so it had less interaction with film components and formed lower flexibility films [12].

The results also showed that when using a G plasticiser, the tensile strength and elastic modulus of the films were the lowest, while the elongation at break was the highest. This proved that the plasticizing ability of G was better than that of PG and PEG 400. This was due to G having a much lower molecular weight than PEG 400, so it was easier to penetrate among polymer chains.

3.4. The WVP of films

The WVP of the HPMC/shellac composite films when using plasticisers at content of 10-30% is summarised in Table 3. The results showed that the WVP of the films with plasticisers was lower than that of the control film without plasticisers. With all plasticisers (G, PG, PEG 400), the films with 20% plasticiser content had a lower WVP than those with 10 and 30% plasticiser content. It is possible that when using 10% content, plasticiser content was not sufficient enough to fully plasticize the film components and thus the components were not uniformly dispersed into each other as indicated in the surface morphology. Therefore, the water vapor resistance of these films was lower. At 20% content, the plasticisers were residual and could combine with itself to open the polymer structure resulting in an increase to the WVP of the film.

Table 3. WVP of films with different plasticisers [g.mm/m².day.kPa].

Plasticiser content (%)	WVP of films		
	G	PG	PEG 400
0	19.65		
10	12.01	11.21	13.79
20	9.87	10.86	11.58
30	11.01	11.56	12.47

Comparing the three types of plasticisers, it was found that when the plasticiser content was 20%, the films using G had the lowest WVP. This might be due to the fact that G has the smallest molecular size, so it could easily penetrate between the polymer chains, so the plasticizing efficiency was higher, and the film components were uniformly dispersed with smaller sizes than PG and PEG 400 plasticisers.

4. Conclusions

Three plasticisers with different concentrations improved the mechanical properties and reduced the WVP of HPMC/shellac composite films. The presence of

plasticisers helped the components of the film to disperse into each other more evenly resulting in a clearer and smoother film surface. Among the three plasticisers, G, PG, and PEG 400, G with a content of 20% was the most effective plasticiser for HPMC/shellac composite films.

CRedit author statement

Thu Trang Pham, Thanh Tung Nguyen, Thi Thu Ha Pham: Conceptualisation, Methodology, Software, Resources, Writing - Review and Editing; Trung Duc Nguyen, Van Khoi Nguyen, Quang Huy Nguyen, Cong Hoan Do: Data curation, Software, Writing original draft preparation; Vu Thang Tran, Thi Phuong Hoang, Phan Hang Nguyen: Supervision, Software, Validation.

ACKNOWLEDGEMENTS

The research was carried out with the financial support of the Institute of Chemistry, Vietnam Academy of Science and Technology under grant number VHH.2021.04.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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