MINISTRY OF EDUCATION AND TRAINING

VIETNAM ACADEMY OF SCIENCE AND TECHNOLOGY

GRADUATE UNIVERSITY OF SCIENCE AND TECHNOLOGY

NGUYEN THI LUONG

RESEARCH ON FABRICATION AND CHARACTERIZATION OF NATURAL POLYMER-BASED COMPOSITES AND THEIR POTENTIAL APPLICATION IN PRESERVATION OF POSTHARVEST FRUIT AND VEGETABLE

Field of Study: Organic chemistry

Code: 9.44.01.14

SUMMARY OF ORGANIC CHEMISTRY DOCTORAL THESIS

Hanoi – 2022

The thesis was completed at Institute of Chemistry - Graduate University of Science and Technology, Vietnam Academy of Science and Technology

Supervisor 1: Dr. Pham Thi Thu Ha
Supervisor 2: Prof., Dr. Nguyen Van Khoi

Reviewer 1:

Reviewer 2:

Reviewer 3:

The thesis shall be defended in front of the Thesis Committee at Academy Level at Institute of Applied Materials Science - Vietnam Academy of Science and Technology at …………….., 2022

The thesis can be found at:

- The National Library of Vietnam
- The Library of Graduate University of Science and Technology

INTRODUCTION

1. The necessity of the thesis

Currently, the oil supply is increasingly exhausted, while the demand is constantly increasing over the years. At the current rate of consumption and the existing oil reserves, this energy source will quickly be exhausted within the next 40-50 years. At the same time, complicated political fluctuations between countries cause oil prices to increase. This significantly affects the cost-economic efficiency and competitiveness of petroleum-based products. Besides, the threat of global warming is also the reason why people are more and more interested in sustainable and environmentally friendly materials.

Since the early years of the 21st century, the world has witnessed a renaissance in renewable polymer sources and a strong development of materials based on natural polymers. It can be said that natural polymers are an ideal replacement for traditional polymers, a source of high economic efficiency, readily available and non-toxic materials. These polymers are chemically modified, highly biodegradable, and some of them are biocompatible.

Along with the development of the agricultural industry in the world as well as issues related to food security, the importance of post-harvest preservation of agricultural products, especially the preservation of fresh fruits and vegetable, increasingly appreciated. Most of the loss in mass and quality of fresh fruits and vegetable takes place in the period from harvest to consumption. It is estimated that post-harvest loss of fruits and vegetable due to spoilage can be as high as 20÷80%. The reason is that fruits after harvest are still living cells and continue to perform respiratory and metabolic activities through a number of transformation processes such as: biochemical change, physical change and chemical change, ... make the fruit ripen quickly, age quickly, and become mushy, leading to spoilage if special measures are not applied to slow down these processes.

Vietnam has a tropical climate, with four seasons all year round, there are products to be harvested. Therefore, the development of post-harvest preservation technologies is of great significance, not only to improve quality and ensure essential nutritional needs for humans, but also to aim for export, bringing economic value to the country.

The technology of fruit and vegetable preservation is being researched and applied quite commonly, which is preservation with edible coatings derived from natural polymers. This coating is applied directly to the surface of vegetable by dipping, spraying, or brushing to create a semi-permeable film. The semi-permeable film formed on the surface of the fruit will limit the process of respiration and control moisture loss, thereby maintaining the quality and extending the shelf life of fresh fruits and vegetable.

On that basis, we have selected the topic of the thesis "***Research on fabrication and characterization of natural polymer-based composites and their potential application in the preservation of postharvest fruits and vegetable***" with the following specific research objectives and content:

2. Research purpose

– Fabrication and characterization of some film composites based on natural polymers.

– Research on potential application of composite based on natural polymers for post-harvest preservation of fruits and vegetable.

3. Research content

– Fabrication and characterization of some film composites based on HPMC/beeswax.
– Fabrication and characterization of some film composites based on HPMC/shellac.
– Research on fabrication of composite films based on HPMC with antibacterial properties.
– Exploratory study on application of composite film based on antibacterial HPMC to preserve fruits and vegetable (seedless lemon, cherry tomato).

CHAPTER 1. OVERVIEW

1.1. Introduction to film-forming materials from biopolymer

Natural polymers are polymers (biopolymers) of natural origin, capable of being degraded by the action of microorganisms such as bacteria, molds, actinomycetes, and enzymes.

Blends or composites of two or more biodegradable polymers can produce a new biodegradable polymer that fit certain requirements. The non-toxic properties and unique biodegradability of biopolymers make them quite popular in the construction industry, cosmetics, paint and ink industries, ... as well as used in packaging, a coating material to protect foods from adverse environmental conditions, keeping them safe and fresh throughout their shelf life. The intended use of natural polymers is changed according to the requirements of the food during storage and preservation.

1.2. Composite film based on hydroxypropyl methyl cellulose

1.2.2. Composite film based on HPMC/Beeswax

In the field of creating films to preserve fruits and vegetable,the most common polysaccharides in polysaccharides are cellulose ethers derived from HPMC, containing both types of functional groups: methoxy group (–OCH_3) and hydroxypropyl group (–OC_3H_6OH), having the ability to change the potential of cellulose ether and give special properties that it is soluble in water and organic solvents.

HPMC-based films are generally flexible, durable, transparent, and stable. However, the moisture barrier properties of HPMC membranes are extremely poor, so to improve this property, many studies have combined lipid components into the films.

Beeswax is the most common lipid commonly used due to its beneficial properties, such as the ability to prevent the formation of chemical free radicals of flavonoids (contains 20-30 types of flavonoids) and contains many nutrients such as vitamins B1, B2, E,...

Beeswax is highly soluble in benzene, toluene, chloroform and other polar organic solvents. Beeswax has the ability to preserve food very well, is difficult to dissolve, smooth, is not chemically affected, limits air permeability and controls moisture.

1.2.3. Composite film based on HPMC/Shellac

Shellac is a natural resin, the chemical composition of which is composed of mono- and polyesters of hydroxy fatty acids (mainly aleuritic acid) and sesquiterpenoid acids (mainly jalaric and laccijalaric acids). Shellac exhibits many useful properties, including excellent film forming, adhesion and glossy coatings. In addition, Shellac is biodegradable and non-toxic. As a result, Shellac has been widely used as a coating for foods, confectionery, solid pharmaceutical dosage forms, and for edible coating materials.

They combined shellac with other materials such as cellulose derivatives: hydroxypropyl methylcellulose (HPMC), carboxymethyl cellulose (CMC), ... and lipid-based materials to increase the advantages and improve the limitations of single materials. Typically, shellac is difficult to dissolve in water, combined with hydrophilic HPMC will overcome this drawback. The rigid and brittle disadvantages of shellac combined with the flexibility of HPMC and plasticizers will increase the flexibility of composites.

1.2.4. Plasticizer

Plasticizers containing –OH groups form hydrogen bonds with biopolymers, and thus increase the free volume and flexibility of the film matrix. Plasticizers that exist in liquid state such as Glycerol, Propylene Glycol, Polyethylene Glycol 400, ... will create stronger interactions between plasticizer molecules and polymer chains than solid plasticizers due to the chain lubricating effect, effective in increasing the free volume and increasing the flexibility of the HPMC/BW and HPMC/Sh polymer molecules.

Usually, the degree of plasticization of this group of substances depends on their chemical structure, including: composition, molecular weight and functional groups. In particular, the compatibility between the polymer and the plasticizer plays an important role in determining the properties of the polymer.

1.2.5. Emulsifier

Emulsifiers are substances that reduce the surface tension of the phases in the system and thereby maintain the structural stability of the emulsion system. In emulsions, the emulsifiers are distributed at the interface between the two phases: the polar end will be in the water phase and the non-polar end will be in the oil phase, towards the oil phase. With the above molecular distribution, the emulsifiers will form a protective layer around the dispersed particles to help the emulsion system be stable. Usually, the emulsifiers used in the formation of natural polymer films are mostly fatty acids, fatty acid esters, alcohols, etc., in which fatty acids such as stearic, lauric, or oleic are often used as emulsifiers. Edible coatings such as HPMC/Sh and HPMC/BW are used in fruit preservation, to overcome brittleness and create high gloss as well as to create the size of small lipid particles in the emulsion system.

1.2.6. Antibacterial additives and antibacterial essential oils

Currently, the antibacterial additives of natural origin are being used commonly and widely such as: green tea, lemongrass essential oil, turmeric essential oil, lemon essential oil, garlic essential oil, ... can all be applied on a number of fruits. Adding natural antibacterial additives also improves antioxidant capacity, controls moisture loss, slows down the darkening of fruits and vegetable, and does not affect the taste of fruits and green materials, eco-friendly green material, easy to biodegrade.

1.2.7. Composite film based on HPMC have antibacterial properties

Currently, the trend of adding natural antibacterial additives to edible coating films is not popular at present, at the same time, the production of edible natural polymer films with antibacterial additives should ensure antibacterial properties (bacteria and fungi, pathogenic yeasts) as well as retain fruit color, moisture and do not reduce weight loss of fruit during storage.

One of the trends in the food industry today is to replace synthetic additives with natural compounds, especially in the field of food preservation. Therefore, the research development of biopolymer films using degradable polymers combined with natural antibacterial agents is one of the highly promising technologies to ensure the quality and safety of food products during storage.

1.3. Preservation of fresh fruits and vegetable by biopolymer film based on HPMC

After harvesting, vegetable and fruits are still living cells and continue to perform respiratory and metabolic activities through a number of transformation processes. It is these changes that make vegetable and fruits ripen quickly, age quickly, become mushy, ... leading to spoilage if special measures are not applied to slow down this process. Currently, the technology of preserving fruits and vegetable that is being researched and used quite commonly is preservation by edible coatings derived from natural polymers. The vegetable selected for preservation are also very diverse such as tomatoes, oranges, grapefruits, litchi, longans, pineapples, persimmons, mangoes, ... Most of the studies show very positive results. In the world, the research and fabrication of composite films combined with different essential oils to improve film properties and antibacterial ability applied in food preservation has also attracted much attention. However, for domestic and foreign fruits, there are differences in ecological regions and quality, leading to differences in preservation methods, temperature or storage time. Therefore, the preservation of fruits with edible films in some projects around the world needs to be surveyed and re-evaluated to be suitable for Vietnamese fruits.

At the same time, in Vietnam, there are many research works to effectively exploit the potential of natural essential oil raw materials for diverse applications in the fields of: pharmaceuticals, food, cosmetics,... Most of the These products all use the antibacterial properties of natural essential oils, but the incorporation of essential oils into edible composite films for post-harvest preservation of fruits and vegetable is still a new research direction that needs to be widely deployed.

CHAPTER 2. EXPERIMENT

2.1. Experiment

Composite films based on HPMC (HPMC/BW, HPMC/Sh), and composite films based on HPMC with antibacterial properties (HPMC/BW/Oregano, HPMC/BW/Thymol, HPMC/Sh/Oregano, HPMC/Sh/Thymol) were fabricated. Properties of composite films were investigated by using modern methods such as: SEM, physico-mechanical, FTIR, OP, DSC, particle size, ...

The HPMC/BW, HPMC/BW/Oregano and HPMC/BW /Thymol composites were used to preserve seedless lemon; the HPMC/Sh, HPMC/Sh/Oregano and HPMC/shellac/Thymol composites were used to preserve cherry tomatoes. The quality control of seedless lemons and cherry tomatoes before and after storage were carried out by determination of damage rate, mass loss, peel color, vitamin C content, total acid content, and respiratory intensity.

2.2. Analytical and evaluation methods

2.2.2. Film analysis and evaluation methods

– Water vapor permeability through the membrane measured by the test cup method according to ASTM E96 – 92.

– Scanning electron microscope (SEM) were imaged by a JEOL SM – 6510 LV at 10–15KV, Japan.

– The physico-mechanical properties of the film were evaluated using Tensilon RTC-1210A and the emulsion particle size was measured by Horiba Laser Scattering Particle Size Distribution Analyzer Partica LA-920, Japan.

– Infrared spectroscopy (FTIR) analysis on Fourier Shimadzu 8400s, Japan.

– Film air permeability was measured with an Illinois Instruments Model 8500 Oxygen permeation analyzer, Spain.

– The glass transition temperature Tg of the film was measured on a DSC 204F1 differential scanning calorimeter, Phoenix, Germany.

– The antibacterial activity of the film was measured according to the standard ASTM E2149-13A, at the Pasteur Institute in HCM City.

2.2.3. Evaluation methods of the quality of fruits and vegetable

– Color measurement of pods using Konica Minolta–CR 400 colorimeter, USA. Respiration intensity was measured using a Dansensor–Ringsted instrument, Denmark.

– Determination of vitamin C content by redox method and total acid by neutralization method.

CHAPTER 3. RESULTS AND DISCUSSION

3.1. Research on fabrication and characterization of HPMC/BW composite films

3.1.1. Effects of HPMC

In this study, the HPMC/BW composite film was made from a composition containing Glycerin (2%); BW (5%), OA (1%), and the content of HPMC varied from 3–7% (3%–B3H, 5%–B5H, 7%–B7H); with the following membrane performance evaluation results:

Composite film 5% HPMC (B5H) has good toughness, elasticity, uniform film surface, beautiful gloss, little breakage, uniform dispersion, no cracks and horny scales inside the structure; the loss of water vapor through the film is the lowest, while achieving good physico-mechanical properties.

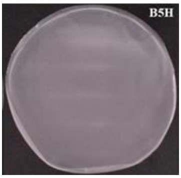


Fig. 3.1. Sensory of HPMC/BW films according to HPMC

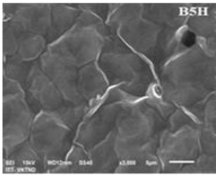


Fig. 3.3. Surface SEM images of HPMC/BW films according to HPMC

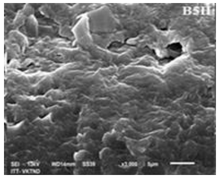


Fig. 3.4. Section SEM images of HPMC/BW films according to HPMC

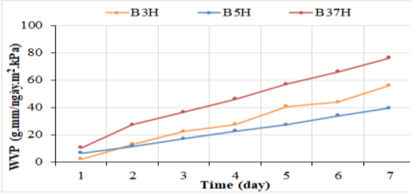


Fig. 3.2. Water vapor permeability of HPMC/BW films according to HPMC

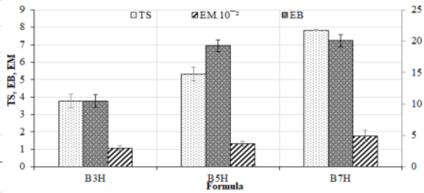


Fig. 3.5. Physico-mechanical properties of HPMC/BW films according to HPMC

3.1.2. Effects of plasticizer

In this study, the HPMC/BW composite film was made from a composition containing HPMC (5%); BW (5%), OA (1%), change of plasticizer type and content ((0%–BKHD); Glycerin (1%–B1G, 2%–B2G, 3%–B3G); Propylene glycol (1%–B1PG, 2%–B2PG, 3%–B3PG); Polyethylene glycol 400 (1%–B1PEG, 2%–B2PEG, 3%–B3PEG)); with the following membrane performance evaluation results:

Glycerol with its compatibility and effective interaction with the -OH groups of the polymer chain enhances the plasticizing effect of the film, film-forming with the lowest moisture resistance, good physico-mechanical properties and improves the air permeability of the HPMC/BW composite film.

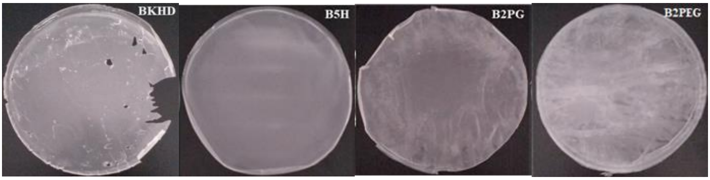


Fig. 3.6. Sensory of HPMC/BW films according to plasticizer

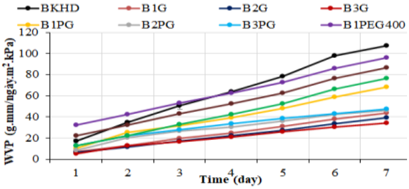


Fig. 3.7. Water vapor permeability of HPMC/BW films according to plasticizer

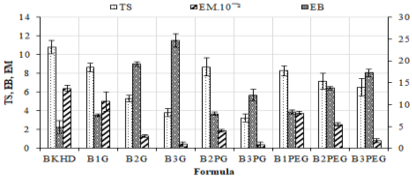


Fig. 3.10. Physico-mechanical properties of HPMC/BW films according to plasticizer

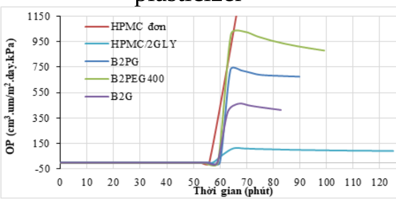


Fig. 3.11. Air permeability of HPMC/BW films according to plasticizer

3.1.3. Effects of beeswax

In this study, the HPMC/BW composite film was made from a composition containing HPMC (5%); Glycerin (2%) and OA (1%), and the content of BW varied from 3–7% (3%–B3BW, 5%–B5BW, 7%–B7BW); with the following membrane performance evaluation results:

The 5% beeswax (B5BW) film has relatively good resistance to water vapor, the film is flexible and tough, and there is no defect in the film structure.

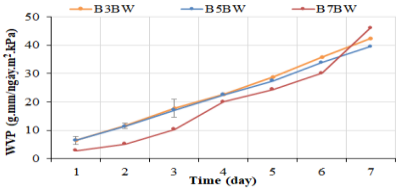


Fig. 3.13. Water vapor permeability of HPMC/BW films according to BW

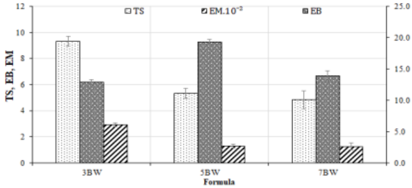


Fig. 3.16. Physico-mechanical properties of HPMC/BW films according to BW

3.1.4. Effects of emulsifier

In this study, the HPMC/BW composite film was made from a composition containing HPMC (5%), Glycerin (2%) and BW (5%), changing the type and content of emulsifier (oleic acid (0.5). %–B0.5OA, 1%–B1OA, 2%–B2OA), lauric acid (0.5%–B0.5LA, 1%–B1LA, 2%–B2LA); stearic acid (0.5%–B0.5SA, 1% –B1SA, 2%–B2SA)); with the following membrane performance evaluation results:

The 1% OA content shows effective emulsification, forming a flexible and elastic film. The Tg value of the HPMC/BW composite film is in the range of Tg of HPMC and BW, showing the suitability in emulsion formulation, stable emulsion system, good dispersion and small average particle size.

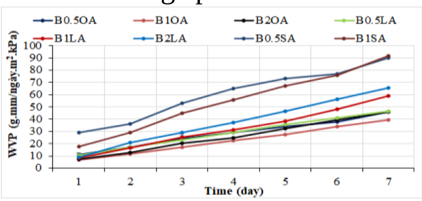


Fig. 3.18. Water vapor permeability of HPMC/BW films according to emulsifier

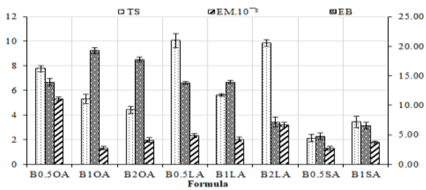


Fig. 3.21. Physico-mechanical properties of HPMC/BW films according to emulsifier

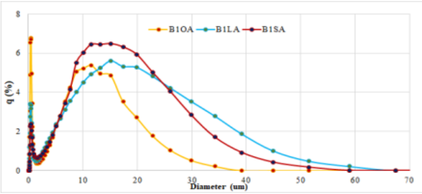


Fig. 3.24. Particle size of HPMC/BW preparations according to emulsifier

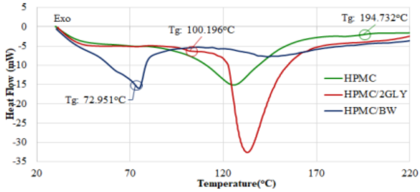


Fig. 3.23. DSC of HPMC/2G and HPMC/BW films

Through evaluation of film properties, it was concluded that the HPMC/BW composite film is made from the following components: HPMC (5%) and Glycerol plasticizer (2%), BW (5%) and OA emulsifier (1%).

3.2. Research on fabrication and characterization of HPMC/Sh composite films

3.2.1. Effects of HPMC

In this study, the HPMC/Sh composite film was made from a composition containing Glycerin (1%), Shellac (0.1%), emulsifier LA (0.01%), and the content of HPMC varied from 3–7 % (3%–S3H; 5%–S5H; 7%–S7H); with the following membrane performance evaluation results:

Composite 5% HPMC, emulsion system creates stable; uniformly dispersed film surface and continuous; the bonds in the membrane structure are less prone to breakage and defects; improve water vapor permeability and enhance physico-mechanical properties.

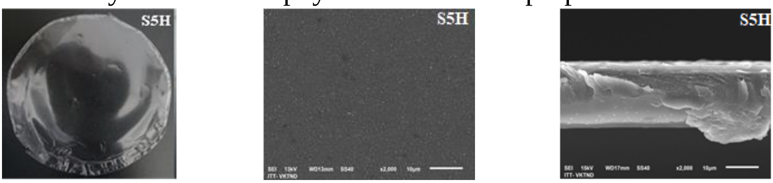


Fig. 3.25. Sensory of HPMC/Sh films according to HPMC

Fig. 3.27. Surface SEM images of HPMC/Sh films according to HPMC

Fig. 3.28. Section SEM images HPMC/Sh films according to HPMC

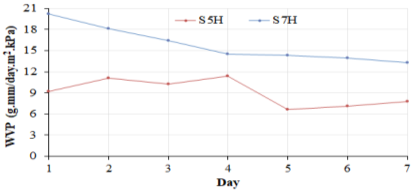


Fig. 3.26. Water vapor permeability of HPMC/Sh films according to HPMC

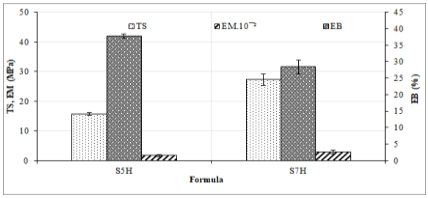


Fig. 3.29. Physico-mechanical properties of HPMC/Sh films according to HPMC

3.2.2. Effects of plasticizer

In this study, the HPMC/Sh composite film was made from a composition with HPMC (5%), Shellac (0.1%) and LA (0.01%) compositions, changing the type and content of plasticizers ((0%——%). BKHD); glycerin (0.5%–S0.5G, 1%–S1G, 2%–S2G); sorbitol (0.5%–S0.5S, 1%–S1S, 2%–S2S); citric acid (0.5%–S0 .5CA, 1%–S1CA, 2%–S2CA)), with the following membrane performance evaluation results:

Composite 5% HPMC, emulsion system creates stable; uniformly dispersed film surface and continuous; the bonds in the membrane structure are less prone to breakage and defects; improve water vapor permeability and enhance physico-mechanical properties.

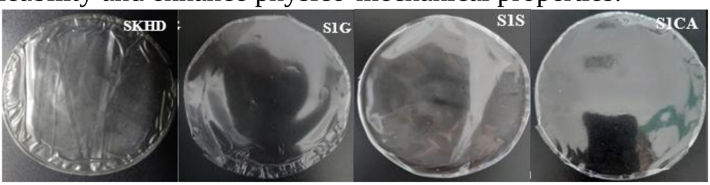
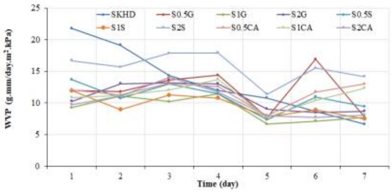


Fig. 3.30. Sensory of HPMC/Sh films according to plasticizer



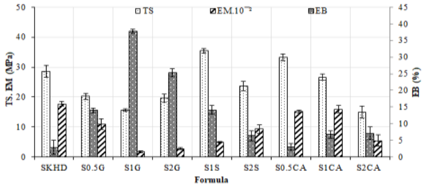


Fig. 3.31. WVP of HPMC/Sh films according to plasticizer

Fig. 3.34. Physico-mechanical properties of HPMC/Sh films according to plasticizer

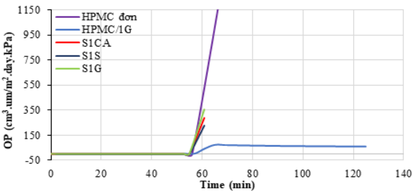
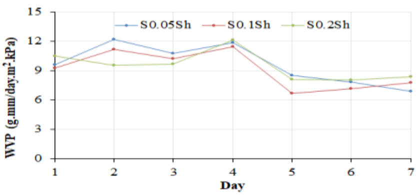


Fig. 3.35. Air permeability of HPMC/Sh films according to plasticizer

3.2.3. Effects of Shellac

In this study, HPMC/Sh composite film was made from HPMC composition (5%); Glycerin (1%) and LA (0.01%), and the content of Shellac varied from 0.05–0.2% (0.05%–S0.05Sh; 0.1%–S0.1Sh; 0.2%–S0.2Sh); with the following membrane performance evaluation results:

The 0.1% Shellac (S0.1Sh) film has relatively good resistance to water vapor, transparent, smooth and flexible, less flawed film.



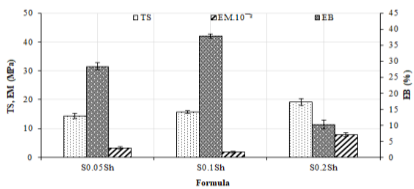


Fig. 3.37. Water vapor permeability of HPMC/Sh films according to Sh

Fig. 3.40. Physico-mechanical properties of HPMC/Sh films according to Sh

3.2.4. Effects of emulsifier

In this study, the HPMC/Sh composite film was made from a composition containing HPMC (5%), Glycerin (1%), Shellac (0.1%), changing the type and content of emulsifier ((0%—— %). SKNH); lauric acid (0.005%–S20LA, 0.01%–S10LA, 0.02%–S5LA); stearic acid (0.005%–S20SA, 0.01%–S10SA, 0.02%–S5SA); with membrane performance evaluation results as follows:

The content of 0.01% LA demonstrates the ability to effectively emulsify to create a film with high homogeneity, so it improves water vapor permeability and has good physico-mechanical properties. The Tg value of HPMC/Sh film is in the range of Tg of HPMC and Sh, showing that the investigation process creates a suitable and stable, a uniform small particle size composite emulsion system.

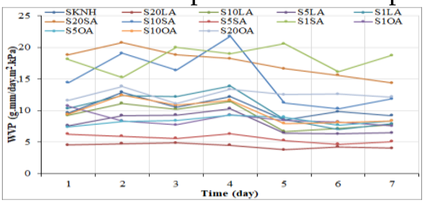


Fig. 3.42. Water vapor permeability of HPMC/Sh films according to emulsifier

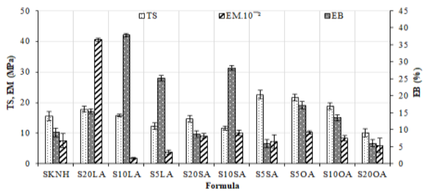


Fig. 3.45. Physico-mechanical properties of of HPMC/Sh films according to emulsifier

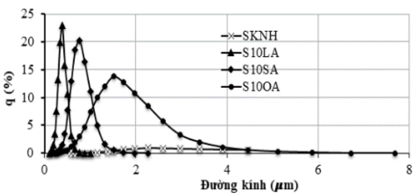


Fig. 3.48. Particle size of HPMC/Sh preparations according to emulsifier

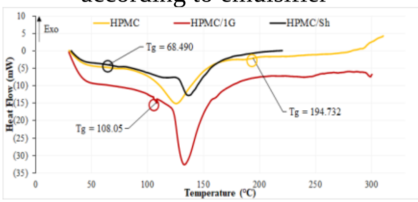


Fig. 3.47. DSC of HPMC/1G and HPMC/Sh films

Through evaluation of film properties, HPMC/Sh composite film was selected which is made from the following components: HPMC

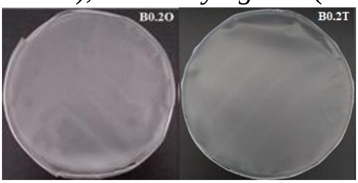
(5%) and Glycerol plasticizer (1%), Sh (0.1%), and LA emulsifier (0.01%).

3.3. Research on fabrication of composite films based on HPMC with antibacterial properties

3.3.1. The composite film based on HPMC/BW/Essential oil

In this study, the composite film HPMC/BW/Essential oil (HPMC/BW/TD) was made from the composition HPMC (5%), glycerin (2%), beeswax (5%) and OA (1). %), change in the type and content of essential oils (oregano (0.1%–B0.1O, 0.2%–B0.2O, 0.3%–B0.3O); thymol (0.1%–B0.1T, 0.2%–B0. 2T, 0.3%–B0.3T)), with the following membrane performance evaluation results:

The 0.2% essential oil composite films are flexible and tough, have good elasticity, the membrane surface is uniform and beautiful, have the ability to resist water vapor, and have similar physico-mechanical properties to the HPMC/BW films, has essential oil components present in the film and is effective against strains of *E.Coli* (Oregano 91.67%/Thymol 83.40%); *S.aureus* (Oregano 96.10%/Thymol 87.80%); *S.typhimurium* (Oregano 91.60%/Thymol 79.17%); *L.monocytogenes* (Oregano 97.38%/Thymol 92.31%).



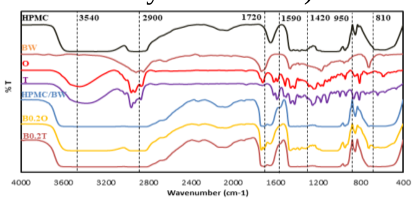


Fig. 3.49. Sensory of HPMC/BW/TD films

Fig. 3.54. FTIR of HPMC/BW/TD films

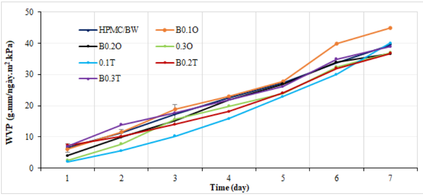


Fig. 3.50. Water vapor permeability of HPMC/BW/TD films

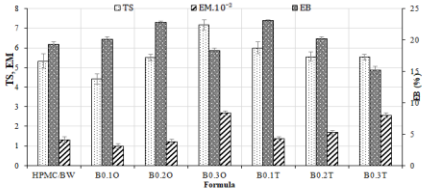


Fig. 3.53. Physico-mechanical properties of HPMC/BW/TD films

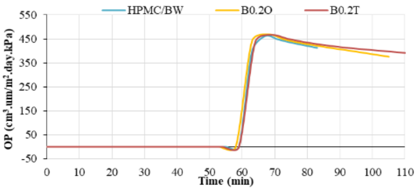


Fig. 3.55. Air permeability of HPMC/BW/TD films

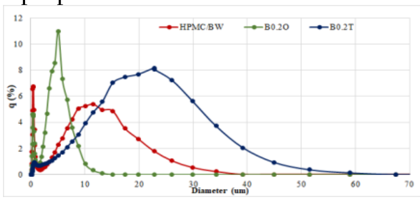


Fig. 3.56. Particle size of HPMC/BW/TD preparations

3.3.2. The composite film based on HPMC/Sh/Essential oil

In this study, composite film HPMC/Sh/Essential oil (HPMC/Sh/TD) was made from the composition HPMC (5%), Glycerin (1%), shellac (0.1%) and LA (0.01%)), change the type and content of essential oil (oregano (0.1%–S0.1O, 0.2%–S0.2O, 0.3%–S0.3O); thymol (0.1%–S0.1T, 0.2%–S0.2T) , 0.3%–S0.3T)); with the following membrane performance evaluation results:

The 0.2% essential oil composite films did not appear with capillaries or cracks in the structure and still created the balance and stability of the HPMC/Sh/TD emulsion system, which was effective against strains of *E.Coli* (Oregano 99.58%/Thymol 99.15%), *S.aureus* (Oregano 98.18%/Thymol 98.10%), *S.typhimurium* (Oregano 99.95%/Thymol 99.95%), *L.monocytogenes* (Oregano 99.98%/Thymol 99.95%).

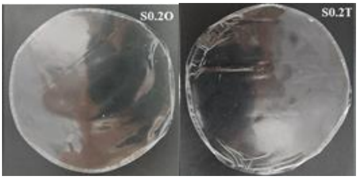


Fig. 3.63. Sensory of HPMC/Sh/TD films

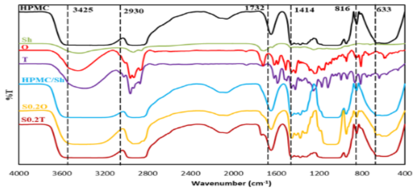


Fig. 3.68. FTIR of HPMC/Sh/TD films

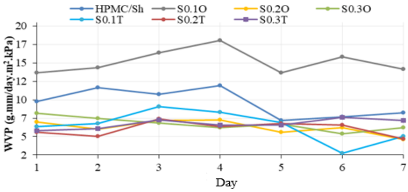


Fig. 3.64. Water vapor permeability of HPMC/Sh/TD films

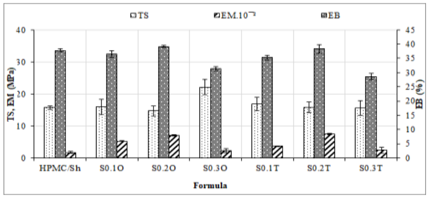


Fig. 3.67. Physico-mechanical properties of HPMC/Sh/TD films

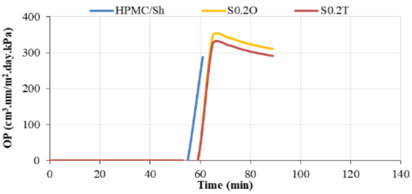


Fig. 3.69. Air permeability of HPMC/Sh/TD films

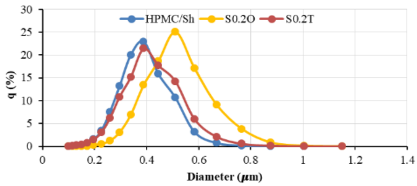


Fig. 3.70. Particle size of HPMC/Sh/TD preparations

3.4. Research on application of HPMC/Shellac/Essential oil films to preserve seedless lemon

The HPMC/BW/Essential oil composite film has the ability to slow down the respiration process of preserved fruit better than the film without essential oil, so the ripening speed of the fruit covered with the essential oil film will also be slower, loss of fruit mass and spoilage rate is the lowest, maintained until day 60, the color of the pods has little change, inhibit the loss of total acid content and avoids the loss of nutrients such as vitamin C.

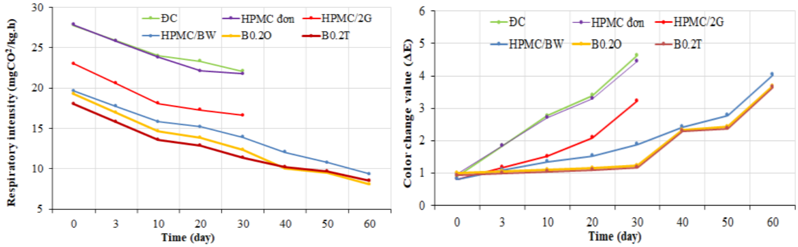


Fig. 3.77. Respiration intensity and rind color change of seedless lemon

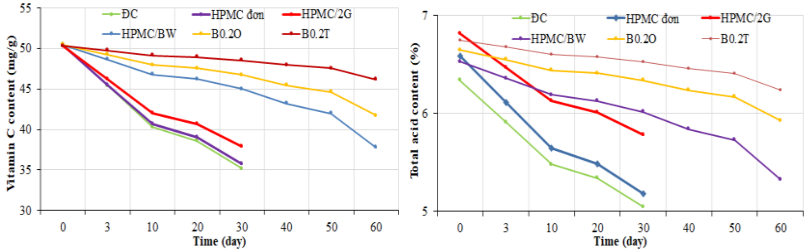


Fig. 3.78. Vitamin C and total acid content of seedless lemon

3.5. Research on application of HPMC/Shellac/Essential oil films to preserve cherry tomatoes

The composite films add essential oils to reduce oxygen consumption and CO2 production due to the lipophilic magnetic gas diffusion of the essential oils, inhibition of respiratory intensity 19 activity and variation in color, the lowest percentage of loss mass and spoilage, maintaining the preservation effect for up to 45 days.

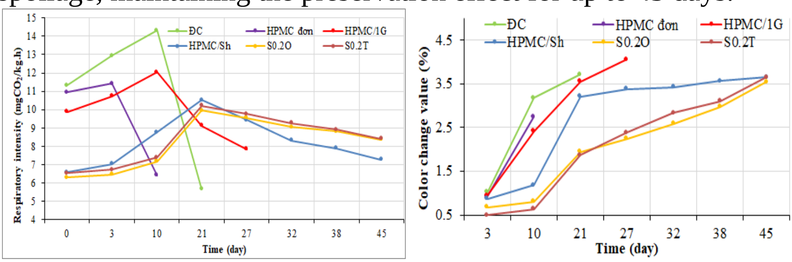


Fig. 3.80. Respiration intensity and rind color change of cherry tomato

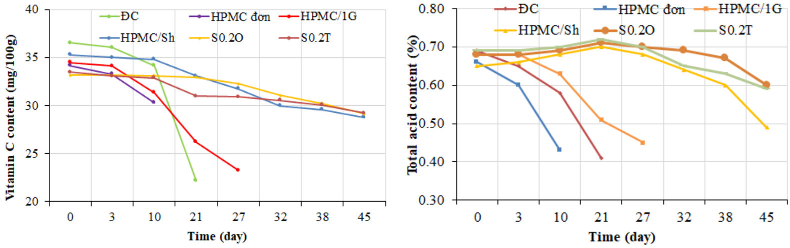


Fig. 3.81. Vitamin C and total acid content of cherry tomato

CONCLUSION

1. HPMC/BW composite membrane has been fabricated with the formula of 5% HPMC, 2% Glycerol, 5% BW and 1% OA outstanding features such as: achieve smooth film surface, uniformly dispersed components, good physico-mechanical properties (tensile strength: 5.32MPa, elongation at break: 19.26% and elastic modulus: 131MPa), water vapor permeability (22.65g.mm/ngày.m^2.kPa), air permeability decreased; have compatibility as well as create emulsions with small particle size, stable (3.85µm).

2. HPMC/Sh composite film has been fabricated with the formula of 5% HPMC, 1% Glycerin, 0.1% Shellac and 0.01% LA to create a film with transparency, flexibility, no fracture, good physico-mechanical properties (tensile strength: 15.72MPa, elongation at break: 37.80% and elastic modulus: 170MPa), water vapor permeability (9.90g.mm/ngày.m^2.kPa), air permeability decreased; have compatibility as well as create emulsions with small particle size, stable (0.3659µm).

3. HPMC/BW/Essential oil composite film has been fabricated with the optimal formula of 5% HPMC, 2% Glycerin, 5% BW, 1% OA, and 0.2% Oregano or Thymol essential oil, creating a film that retains the same outstanding features as the HPMC/BW composite film. However, with the presence of essential oil components, was effective against strains of E.Coli (Oregano 91.67%/Thymol 83.40%), S.aureus (Oregano 96.10%/Thymol 87.80%), S.typhimurium (Oregano 91.60%/Thymol 79.17%), L.monocytogenes (Oregano 97.38%/Thymol 92.31%).

4. HPMC/Sh/Essential oil composite film has been fabricated with the optimal formula of 5% HPMC, 2% Glycerin, 5% BW, 1% OA, and 0.2% Oregano or Thymol essential oil, creating a film that retains the same features as the HPMC/Sh composite film. Especially with the presence of essential oils, was improved effectiveness against strains of E.Coli (Oregano 99.58%/Thymol 99.15%), S.aureus (Oregano 98.18%/Thymol 98.10%), S.typhimurium (Oregano 99.95%/Thymol 99.95%), L.monocytogenes (Oregano 99.98%/Thymol 99.95%).

5. Exploration and application of beeswax composite film to preserve seedless lemons at conditions of 8–10ºC; humidity 90–95%. Based on the evaluation of the quality of seedless lemons after storage, HPMC/BW, HPMC/BW/Thymol and HPMC/BW/Oregano films can last up to 60 days.

6. Exploration and application of shellac composite membrane to preserve cherry tomatoes at conditions of 10–12ºC; humidity 90–95%. Evaluation of the quality of cherry tomatoes after storage showed that HPMC/Sh and HPMC/Sh/Thymol and HPMC/Sh/Oregano films could last up to 45 days.

THE NEW CONTRIBUTED POINTS OF DISSERTATION

Successfully fabricated composite film products HPMC/Beeswax, HPMC/Shellac, HPMC/Beeswax/Oregano, HPMC/Beeswax/Thymol, HPMC/Shellac/Oregano and HPMC/Shellac/Thymol achieving the superior characteristics, structural properties, and morphology such as air permeability, gloss, durability, antibacterial ability... compared to single-component films.

Fabricated preparations of edible coatings, with improved features, have been produced in the form of an aqueous emulsion that is safe in production and use and does not require drying fruits and vegetables before coating. Simultaneously extend the shelf life of seedless lemons to 60 days and cherry tomatoes to 45 days.

The results will promote the exploitation and effective use of available materials shellac, beeswax to create edible coatings and expand application in other fields using safety films: cosmetics, and pharmaceuticals.

PUBLISHCATION LIST

1. Pham Thi Thu Ha, **Nguyen Thi Luong**, Ho Xuan Huong, Nguyen Van Khoi, Nguyen Thanh Tung (2019). Effect of plasticizer on properties of composite films from HPMC/Shellac. *Vietnam Journal of Chemistry*, 57(6E12), 140–146.
2. **Nguyen Thi Luong**, Do Kim Nhung, Pham Thi Thu Ha, Nguyen Van Khoi, Nguyen Thanh Tung (2019). Mechanical properties, morphology, and water vapor permeability of HPMC/Shellac composite films. *Vietnam Journal of Chemistry*, 57(6E12), 436–441.
3. **Nguyen Thi Luong**, Nguyen Dinh Dung, Hoang Xuan The, Le Thi Hong Thuy, Nguyen Pham Khanh Van, Nguyen Thi Ky Anh, Vu Thi Huong Lan, Vo Thi Phương Trang (2019). Research properties and *Staphylococcus aureus* bacterial resistance of HPMC/Beewax composite films combination with Thymol. *Scientific Conference Food Safety and Food Security*, 3rd, 373.
4. **Nguyen Thi Luong**, Nguyen Hoc Thang, Nguyen Van Khoi, Pham Thi Thu Ha, Le Thi Hong Thuy, Nguyen Thanh Tung (2020). Characteristics of HPMC/Beeswax Edible Composite Film and Its Application for Preservation of Seedless Lime Fruit. *Key Engineering Materials*, 850, 87–93.
5. **Nguyen Thi Luong**, Nguyen Pham Khanh Van, Nguyen Hoc Thang, Nguyen Van Khoi, Pham Thi Thu Ha, Nguyen Thanh Tung (2021). Effects of Plasticizers on Mechanical Properties, Oxygen Permeability, and Microstructural Characteristics of HPMC/Beeswax Composite Film. *Nano Hybrids and Composites*, 32, 25–34.
6. **Nguyen Thi Luong**, Nguyen Thanh Tung, Pham Thi Thu Ha, Nguyen Van Khoi, Nguyen Pham Khanh Van, Le Thi Hong Thuy (2021). Effects of Plasticizers on Structures of Chemical Functional Groups, Morphologies, Water Vapor Permeability, and Thermal Properties of HPMC/BW Biopolymer Films. *Journal of Polymer & Composites*, 9(2), 10–20.
7. Vu Thi Huong, Le Thi Hong Thuy, Nguyen Hoc Thang, Nguyen Thanh Tung, Nguyen Van Khoi, Pham Thi Thu Ha, Truong Ngoc Yen, **Nguyen Thi Luong** (2021). Effect of Emulsifiers on Engineering and Microstructural Properties of HPMC/Shellac Composite Films. *Material Science Forum*, 1051, 181–188.