DOI: 10.31276/VJSTE.62(4).18-22

Pectin bioplastic films regenerated from dragon fruit peels

Thi Cam Trang Truong[1*], **Takaomi Kobayashi**[2]

[1]*Faculty of Environmental Sciences, University of Science, Vietnam National University, Ho Chi Minh city, Vietnam*
[2]*Department of Science of Technology Innovation, Nagaoka University of Technology, Japan*

Received 17 August 2020; accepted 10 November 2020

Abstract:

Pectin extracted from dragon fruit peels was used to prepare pectin-based membranes by mixing with the plasticized agent polyethylene glycol (PEG) at pectin to PEG ratios of 5:1, 3:1, and 1:1. SEM images showed the resulting bioplastic films had a transparent yellowish surface without pores or cracks. The water content of the bioplastic films was 29.17, 48.61, and 59.72% for the 5:1, 3:1, and 1:1 ratios, respectively. This showed that the increase in PEG concentration made the bioplastic films weaker and more hydrophilic. The tensile strength of films was 5.0, 4.9, and 2.5 N/mm^2 and the value of optical transmittance was 18, 19, and 24%, for the 5:1, 3:1, and 1:1 ratios, respectively. The significant decrease in tensile strength is attributed to the high concentration of PEG, which lead to the clustering in the material's structure. Therefore, these bioplastic films are applicable to the highly suitable and stable operations of packing materials in the food and medical industries.

Keywords: **bioplastic film, dragon fruit, pectin, polyethylene glycol.**

Classification number: **5.1**

Introduction

Over the past 20 years, the large-scale production and utilization of plastic all over the world has increased dramatically, which entails the issue of waste disposal [1]. In this sense, research on biodegradable films prepared from polysaccharides has been on the rise, which establishes these biopolymers as potential candidates for biodegradable film production [2].

According to the organization European Bioplastics, bioplastics are defined as materials based on renewable resources or those that are biodegradable or compostable [3]. Bio-based plastics are made from polysaccharides such as starches, cellulose, chitin, pectin, proteins like wheat gluten, wool, silk, gelatin, lipids (animal fats), vegetable oils, and products of microorganisms. Pectin is a natural material that appears in a great proportion of fruits and vegetables such as berries, apples, and oranges. Pectin is a mandatory polymer and its use in industry has diverse applications that continues to grow [2]. Pectin is a necessary component in plant cell structure and it consists of α-(1, 4)-linked D-galacturonic acid residues in which a part of the galacturonic acid is esterified or an acetylated methyl or both [4]. Depending on the degree of esterification (DE), pectin is divided into high-methoxyl (HM) pectin (DE>50%) and low-methoxyl (LM) pectin (DE<50%) [5]. Pectin extraction is typically performed by way of solvent extraction from raw materials where all extraction conditions, such as extraction temperature, extraction time, pH, and type of extraction solvent can affect the yield and quality of extracted pectin [4]. Normally, solvents with strong hydrogen bonding capacity are good for polysaccharides [6], which could promote carbohydrate chain spreading. Pectin molecules with a completely extended structure in a good solvent have better steric impediment, which stands in the way of intermolecular flocculation. Pectin has attracted a lot thanks to its exceptional properties; they are able to freeze in the presence of acids and sugars, have a high viscosity, are

---

[*] *Corresponding author: Email: ttctrang@hcmus.edu.vn*

an aqueous-absorbent gel, and easily soluble in water but insoluble in ethanol. Due to the features mentioned, pectin represents a potential polymer for the development of bio-based membranes in the food packaging field [7].

Recently, dragon fruit or pitaya has become a popular fruit due to its attractive appearance and nutrition. It can be processed into a variety of food products such as juice, jam, ice cream, or yogurt. Dragon fruit peel, with up to 39% pectin, instantly becomes a convenient and attractive choice for pectin extraction. In addition, previous research has shown that dragon fruit peel can be used as a raw material for pectin extraction [4]. Like most of the polysaccharides, pectin is glassy in its normal condition, so shrinkage due to water evaporation or swift drying causes defects such as cracks or curling in the films. These films are often brittle and stiff because of extensive interactions between polymer molecules, so the addition of the corresponding plasticizers is required. Plasticizers act by interposing themselves between macromolecular polymeric chains, which reduces cohesion within the film and enhances the free volume inside the film structure [7]. With reference to other reports of polysaccharide-based films, it has been shown that PEG of lower molecular weight exhibits an improved plasticizing effect. PEG is non-toxic, odorless, neutral, slippery, non-volatile, and completely soluble in water, but the solubility decreases with increasing polymer molecular weight. PEG is a non-toxic compound and can be used in pharmaceuticals and food additives (Fig. 1).

Materials and methods

Materials

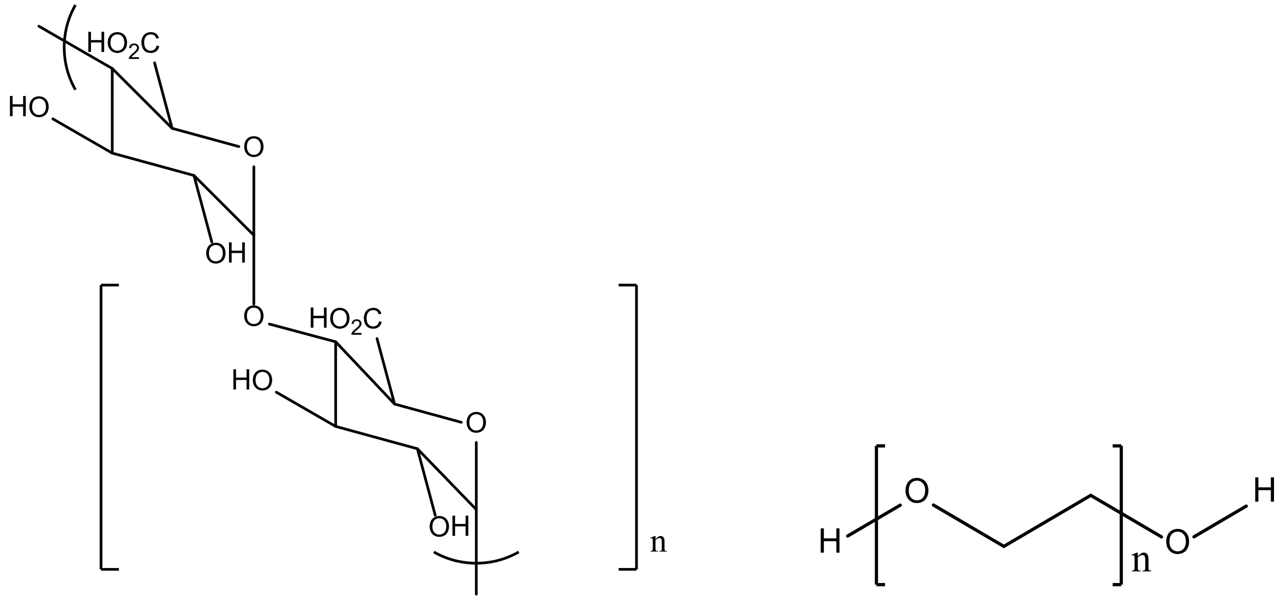
Fresh dragon fruit peel was collected from solid waste in the Ninh Thuan province, Vietnam. The peels were cut into small pieces and dried at 60°C for 36 h. Chemicals used in the extraction of pectin and preparation of bioplastic membrane such as hydrochloric acid (HCl) and ethanol were supplied by Xilong Chemical Reagent Co., Ltd, China while PEG (400 g/mol) was purchased from LAXOPEG Co., Ltd, India.

Pectin extraction

Pectin from dragon fruit peel was extracted using a method modified from [4]. Specifically, 30 g of the dried dragon fruit peel was added to a mixture of 0.1 M hydrochloric acid in 250 ml of distilled water where the pH was adjusted to 3. The extraction process was carried out at 70°C for 30 min while stirring constantly. The final product was obtained by precipitation with a solvent of 2:1 ethanol-to-pectin. Finally, the precipitate was washed with 45% aqueous ethanol solution and dried in an oven at 50°C for 6 h.

Bioplastic film synthesis

The films were made by mixing pectin from the previous work with PEG at various ratios (5:1, 3:1, and 1:1) while stirring continuously for 30 min [8]. After that, the obtained solution was poured into a petri dish (100x15 mm) and



(A) (B)

Fig. 1. Chemical structure of (A) pectin and (B) PEG.

dried at 50°C in 72 h. The film's formation is primarily established between the hydrogen bonds of pectin and PEG with carbonyl groups (C-O), methyl ester ($COOCH_3$), and oxygen atoms from PEG. By adding PEG to the pectin solution, the intermolecular forces in the polymer chain of pectin is reduced owing to an increase in their flexibility and scalability [7].

Characteristics of extracted pectin and pectin-based bioplastic materials

Fourier-transform infrared spectroscopy (FT-IR): FT-IR spectra was used to determine the unknown material, the quality and consistency of the sample, and to quantify the composition of the mixture. The spectra were recorded in the central infrared region (4000 to 400 cm^{-1}) with a resolution of 4 cm^{-1} in absorption mode for 8 to 128 scans at room temperature [9]. After the bioplastic films were made, the FT-IR spectra were measured at the Laboratory of Bio Sustainable and Environmental Materials Engineering, Faculty of Materials Science and Engineering, Nagaoka University of Technology, Japan.

Scanning electron microscopy (SEM): scanning electron microscopy was used to study the morphology of the surface and the cross section of the samples. In the measurement, the samples were fractured in liquid nitrogen and the fractured part was coated with a conductive layer of sputtered gold. The surface and cross section of the samples were investigated using a JSM-5300LV (JEOL, Japan) at the Laboratory of Bio Sustainable and Environmental Materials Engineering, Faculty of Materials Science and Engineering, Nagaoka University of Technology, Japan.

Equilibrium water content (EWC): EWC was measured at room temperature by comparing the initial weight of the dried material to that after immersion in distilled water in continuous intervals of 1 to 6 h and after 12 h. The EWC value was calculated by the following equation: $EWC=(m_2-m_1)/m_1x100$, where m_1 is the initial weight and m_2 is the weight after immersion in distilled water for a particular time.

Water permeability: water permeability indicates the ability to allow water to pass through the material, which was investigated by placing a sample with 9 cm diameter on the outer edge of a 7.5 cm diameter beaker. Then, certain amounts of distilled water were dripped onto the surface of the sample and the quantity of water passing through the other side was measured after 12 h. The dehumidification ability was carried out by drying the material and weighing it until the mass was constant.

Optical transmittance: the optical transmittance (T) is defined as the ratio of the proportion of light that passes through a sample (P) to the amount of light illuminated on the sample (incident light, P_0). This is an important criterion to determine the quality of a bioplastic membrane, especially one used for food packaging. The greater the transmittance is, the faster food decays. The transmittance was measured by cutting the membrane in such a way that it fit a cuvette filled with distilled water. The conducting photometric measurement at 660 nm by UV-Vis spectrophotometer was calculated by the following formula: $A=-\log T=-\log P/P_0$.

Tensile strength: tensile strength of bioplastic films was carried out by a QC-528M1F device, Ometech, at the Ho Chi Minh City Department of Standards Metrology and Quality. Cross-sectional area of samples of known width (10 mm) and thickness (0.1 mm) were used in the calculations. The value of the tensile strength was calculated by using the following equation:

$$\text{Tensile strength} = \frac{\text{maximum load}}{\text{cross-section area}}\ (\text{N/mm}^2)$$

Results and discussion

Pectin extracted from dragon fruit peel has a light pink and yellowish color simply because the betacyanin pigment of dragon fruit was not completely removed (Fig. 2A). The efficiency of this process was 18% and the pectin obtained from it was a low methoxyl pectin with a degree of esterification of 36%. When this is compared with pectin extracted from citrus peel (21.85%) [10] and custard apple peel (8.93%) [11], it is clearly seen that pectin from the dragon fruit peel is an alternative available source that has potential for practical production and application. The productivity of the material preparation process was 116%. The newly molded bioplastic film had a light pink, yellowish hue due to incomplete removal of the betacyanin pigment. Nonetheless, after drying at 50°C for 72 h (Fig. 2B), the film slightly yellowed, which can be explained by the fact that the betacyanin pigment partially decomposed during

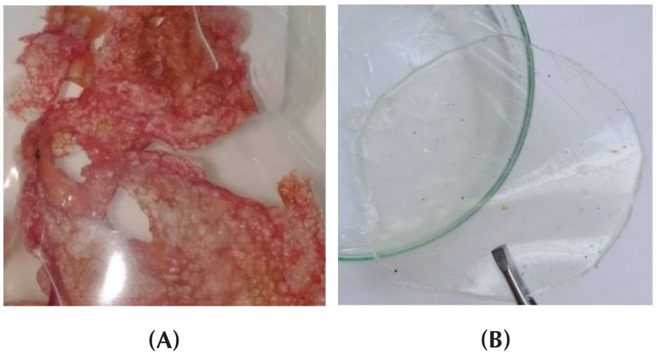

(A) (B)

Fig. 2. (A) Extracted pectin and (B) the pectin-based film.

the heating process. The resulting films were transparent, flexible, and glossy.

Two functional groups were extracted from pectin: the carbonyl group (CO) at 1600 cm^{-1} and the hydroxyl group (OH) at 3200-3600 cm^{-1}. In addition, the carboxyl group (COOH) appeared between 1740-1760 cm^{-1}. Similarities between the functional groups found in the FT-IR spectra of the pectin extracted from dragon fruit peel and that of commercial pectin prove that pectin was successfully extracted [12]. Fig. 3 shows the FT-IR spectra of the bioplastic materials. Specifically, strong absorption bands occurred at 2111 and 1647 cm^{-1}, which refer to carbonyl ester groups (-$COOCH_3$) and the asymmetric prolonged vibration of carboxylate ions (COO^-), respectively. The peaks observed at 1457, 1251, and 1096 cm^{-1} represent the symmetrical elongation fluctuations of C-O-C, C-OH, and C-C links from the structure of pectin, respectively. The observed peaks in the bioplastic film spectra can be attributed to the interaction between pectin and PEG through the formation of hydrogen bonds established between the carbonyl (CO), methyl ester ($COOCH_3$) groups, and oxygen from PEG [7].

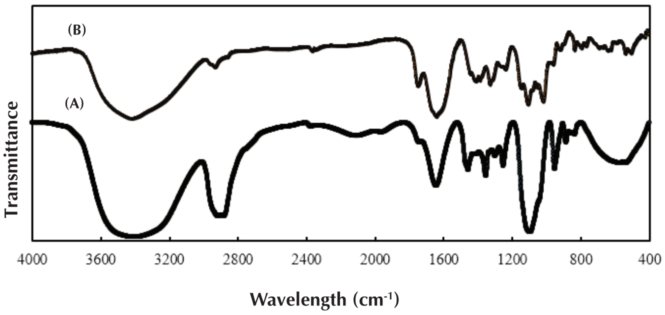
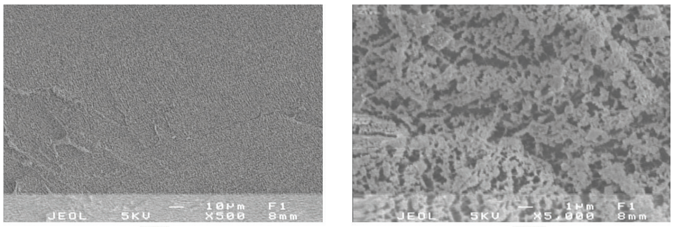


Fig. 3. FT-IR spectra of (A) extracted pectin and (B) bioplastic membrane.

From Fig. 4A, it was obvious that the surface of the bioplastic material was near homogeneous and without pores or cracks. However, there were some signs of fragmentation as seen in Fig. 4B, which were thought to be poorly mixed pectin and PEG, however, this did not affect the structure or morphology of the material. The surface image showed that the bioplastic had a dense structure on the surface.



x500

(A)

x5000

(B)

Fig. 4. SEM picture of the surface bioplastic (5:1) at (A) magnification ×500 and (B) magnification ×5000.

The EWC of the films increased gradually by the time of immersion. In terms of the 5:1 and 3:1 ratio films, after 5 h of saturation, their efficiency was 29.17 and 48.61%, respectively. Meanwhile, the 1:1-ratio film reached equilibrium after 6 h and its efficiency reached 59.72%. It was also noticed that the concentration of PEG increased, which lead to an increase in water uptake capacity. This can be explained by the fact that PEG is slightly hygroscopic [7]. It is well documented that the 5:1-ratio film had the least water retention compared to the others. In other words, the mechanical strength of the films was quite good. Thus, according to the results presented in Table 1, the expansion of the film reached a maximum value of 8.33% within 3 h for the 5:1-ratio film and the diameter of the film increased slightly. For the 3:1-ratio film, the swelling level reached its peak of 10% after 3 h. Similarly, the swelling degree of the 1:1-ratio film was 13.33% after 4 h of hydration. On the other hand, data from the permeability test showed that all of the bioplastic films completely dissolved after 1 h with mechanical agitation. The permeability test outcome illustrated that no phenomenon of water passed from the top to the bottom of the bioplastic films after 12 h for all 3 ratios.

Table 1. The characteristics of pectin-based membranes at different ratios.

	Tensile strength (N/mm^2)	Moisture value (%)	Optical transmittance (%)	Water content (%)	Elongation (%)
1:1	2.5	18.18	24	29.17	8.33
3:1	4.9	9.1	19	48.61	10.00
5:1	5	4.5	18	59.72	13.33

Optical transmittance is one of the most important parameters to evaluate material quality for food packaging. In addition, UV rays can cause lipid oxidation and 660 nm wavelength light can create an environment for microorganisms to grow and cause food spoilage. The results showed that the optical transmittance of all 3 films were quite small; 18, 19 and 24% for the 5:1, 3:1, and 1:1, respectively. The 5:1-ratio film had the smallest value (18%), which is very suitable for packaging and preserving food. In contrast, the film with 1:1 ratio had the largest optical transmittance (24%) because of the slight water absorption property. Based on Table 1, it can easily be seen that after 12 h in atmosphere, the bioplastic films were slightly hygroscopic. When the PEG concentration increased, the hygroscopic moisture of the bioplastic films also increased. This can be explained by the fact that PEG is slightly hygroscopic. The film with the 5:1 ratio of pectin to PEG had the lowest value of hygroscopic property (4.5%). On the other hand, the tensile strength of the bioplastic films was 5 N/mm^2, 4.9 N/mm^2, 2.5 N/mm^2 for the 5:1, 3:1, and 1:1 ratios, respectively. The significant decrease in tensile strength was due to the high concentration of PEG, which lead to clustering in the material's structure. Therefore, the bioplastic films in this study are applicable and highly suitable for packing materials in the food and medical industries [3, 13].

In the present work, pectin-based bioplastic films regenerated from dragon fruit peel showed the most stability and beneficial properties when the ratio of pectin to PEG was 5:1. The pectin extraction yield from the dragon fruit peel, as well as the mechanical and chemical properties of the bioplastic films in the present work, showed a higher value than that from a similar recent study [14]. This may be due to using PEG as the cross-linking agent instead of ethylene glycol. There exist bioplastic films regenerated from apple peels [7], citrus medica [10], and custard apple [11], and all films showed good thermal stability, tensile strength, etc., as packing materials. Therefore, pectin-based bioplastic films regenerated from dragon fruit peels are promising as novel films for food and medical industry packaging in the near future.

Conclusions

The present work has shown success in the extraction of pectin from dragon fruit peel with the production of long, strong, and high quality threads of pectin during coagulation. The results of this study showed that bioplastic films with a 5:1 ratio of pectin to PEG had the best results: the saturated hydration time was 5 h with an efficiency of 29.17% and 5 N/mm^2 of the maximum tensile strength, futherrmore, the value of optical transmittance was 18 after 12 h showed that the increase in Pectin concentration made the membranes stronger and tended to be more hydrophilic. These results prove the environmentally friendly bioplastic films are beneficial in food and medical packaging applications in the near future.

COMPETING INTERESTS

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

REFERENCES

[1] Maurizio Avella, Jan J. De Vlieger, Maria Emanuela Errico, Sabine Fischer, Paolo Vacca, Maria Grazia Volpe (2005), "Biodegradable starch/clay nanocomposite films for food packaging applications", *Food Chemistry*, **93**, pp.467-474.

[2] Teresa I.A. Gouveia, Krzysztof Biernacki, Maria C.R. Castro, Maria P. Gonçalves, Hiléia K.S. Souza (2019), "A new approach to develop biodegradable films based on thermoplastic pectin", *Food Hydrocolloids*, **97**, pp.105-175.

[3] Nanou Peelman, Peter Ragaert, Bruno De Meulenaer, Dimitri Adons, Roos Peeters, Ludwig Cardon, Filip Van Impe, Frank Devlieghere Trends (2013), "Application of bioplastics for food packaging", *Food Science and Technology*, **32**, pp.128-141.

[4] Nudthabong Tongkham, Boonyawee Juntasalay, Patareeya Lasunon, Nipaporn Sengkhamparn (2017), "Dragon fruit peel pectin: microwave-assisted extraction and fuzzy assessment", *Agricultural and Natural Resourses*, **51(4)**, pp.262-267.

[5] Shahrooz Rahmati, Aminah Abdullah, Oon Lee Kang, Bioact (2019), "Yellow passion fruit rind - a potential source of low-methoxyl pectin", *Carbohydr. Diet. Fibre*, **100**, pp.100-186.

[6] Eleftheria Antoniou, C. Francisco Buitrago, Marina Tsianou, Paschalis Alexandridis (2010), "Solvent effects on polysaccharide conformation", *Carbohydrate Polymers*, **79**, pp.380-390.

[7] Sanja Šešlija, Aleksandra Nešić, Jovana Ružić, Melina Kalagasidis Krušić, Sava Veličković, Roberto Avolio, Gabriella Santagata, Mario Malinconico (2017), "Edible blend films of pectin and poly (ethylene glycol): preparation and physico-chemical evaluation", *Food Hydrocolloids*, **77**, pp.494-501.

[8] Basma Y. Alashwal, Mohamed Saad Bala, Arun Gupta, Swati Sharma, Puranjan Mishra (2019), "Improved properties of keratin-based bioplastic film blended with microcrystalline cellulose: a comparative analysis", *Journal of King Saud University - Science*, **32**, pp.853-857.

[9] Tuspon Thanpitcha, Anuvat Sirivat, Alexander M. Jamieson, Ratana Rujiravanit, J. Nanopart Res (2009), "Polyaniline nanoparticles with controlled sizes using a cross-linked carboxymethyl chitin template", *Journal of Nanoparticle Research*, **11**, pp.1167-1177.

[10] Bahare Pasandide, Faramarz Khodaiyan, Zeinab E. Mousavi, Seyed Saeid Hosseini (2017), "Optimization of aqueous pectin extraction from *Citrus medica* peel", *Carbohydrydrate Polymers*, **178**, pp.27-33.

[11] C.S. Shivamathia, I. Ganesh Moorthya, R. Vinoth Kumarb, Michael Rahul Soosaia, J. Prakash Maranc, R. Shyam Kumara, P. Varalakshmid (2019), "Optimization of ultrasound assisted extraction of pectin from custard apple peel: potential and new source", *Carbohydrate Polymers*, **225**, DOI: 10.1016/j.carbpol.2019.115240.

[12] J.M. Joel, J.T. Barminas, E.Y. Riki, J.M. Yelwa, F. Edeh (2018), "Extraction and characterization of hydrocolloid pectin from Goron Tula (Azanza garckeana) fruit", *World Scientific News*, **101**, pp.157-171.

[13] Azwan Mat Lazim, Farahain Mokhtar, Siti Fairus Mohd Yusof, Ishak Ahmad, Adil Hakam (2013), "Synthesis and characterization of pH sensitive hydrogel using extracted pectin from dragon fruit peel", *Malaysian Journal of Analytical Sciences*, **17**, pp.481-489.

[14] Risnita Vicky Listyarini, Puspita Ratna Susilawatib, Esther Natalia Nukung, Maria Anastasia Toyo Yuaa (2020), "Bioplastic from pectin of dragon fruit (Hylocereus polyrhizus) peel", *Malaysian Journal of Analytical Sciences*, **23(6)**, pp.203-208.