UJAT
Universidad Juárez Autónoma de Tabasco
"Estudio en la duda. Acción en la fe"

División Académica de Ciencias Básicas
UJAT

JOBS Journal of Basic Sciences

DACB • UJAT

Volumen 10 • número 28 • mayo-agosto 2024

ISSN:2448-4997
https://revistas.ujat.mx/index.php/jobs

OPEN ACCESS

UJAT
Universidad Juárez Autónoma de Tabasco
"Estudio en la duda. Acción en la fe"

Básicas UJAT

JOBS Journal of Basic Sciences
DACB UJAT

Es grato entregar a los lectores el número 28 del Journal of Basic Sciences, en donde se han integrado reportes de investigación alrededor de diferentes temáticas, con aspectos que cubren la búsqueda de estrategias sostenibles, el desarrollo de la ciencia de los materiales y aportaciones dirigidas a la enseñanza de las ciencias. Así, se presenta el desarrollo de una propuesta para la síntesis de bioplásticos a partir de un desecho agroindustrial como lo es la pectina, la cual se considera un recurso renovable y de fácil acceso. Mediante una serie de transformaciones químicas, se logró la obtención de un material polimérico con propiedades apropiadas para procesos térmicos. Por otro lado, ante la problemática derivada de una gestión inadecuada de residuos plásticos, se cuenta con estrategias de reciclaje de este tipo de materiales, con lo que se logran beneficios tanto al medio ambiente como a la economía, derivado de lo anterior, se desarrolló un estudio para reciclar polietileno de alta densidad para generar soportes que pueden ser empleados en la reparación de mobiliario escolar, proponiendo así una alternativa viable para reducir los residuos plásticos, obteniendo un material práctico con un gran potencial de utilidad. La ciencia de los materiales persigue el diseño y obtención de nuevas sustancias destinadas a cumplir funciones específicas, en función de un diseño apropiado de sus propiedades, en este tenor, se presenta un reporte para la obtención de materiales híbridos preparados a partir de grafito convenientemente tratado, con la finalidad de obtener electrodos para supercondensadores, que puedan tener una alta capacidad de almacenamiento energético. Este proceso se describe como económico y con la ventaja de poder ser realizado en un tiempo relativamente corto. Continuando con el diseño de nuevos materiales, se presenta la obtención de zeolitas modificadas con cobre mediante un proceso mecanoquímico. Este tipo de modificaciones permite generar propiedades novedosas, con aplicaciones inusuales. En el reporte incluido en este número, se describe la preparación de la zeolita modificada, su caracterización estructural y la comparación contra el material original, con la finalidad de estudiar el efecto del proceso aplicado. En otro orden de ideas, se incluye una contribución que explora el desarrollo de un recurso didáctico para aplicarlo en el aprendizaje de la química. Específicamente, se propone una estrategia lúdica basada en un cómic para facilitar la adquisición de conocimientos relacionados con la simetría molecular. Al mostrar diferentes facetas en donde se ve involucrado el desarrollo de las ciencias básicas, se espera que este número cumpla con las expectativas y resulte de interés para la comunidad de lectores del Journal of Basic Sciences.

ISSN:2448-4997
https://revistas.ujat.mx/index.php/jobs

DIRECTORIO INSTITUCIONAL

Universidad Juárez Autónoma de Tabasco

- Lic. Guillermo Narváez Osorio. Rector
- Dr. Luis Manuel Hernández Govea. Secretario de Servicios Académicos
- Dr. Wilfrido Miguel Contreras Sánchez. Secretario de Investigación, Posgrado y Vinculación
- Dr. Pablo Marín Olán. Director de Difusión, Divulgación Científica y Tecnológica

Directorio Divisional

División Académica de Ciencias Básicas

- Dra. Hermicenda Pérez Vidal. Directora
- Dr. Luis Manuel Martínez González. Coordinador de Investigación
- M.C. Abel Cortazar May. Coordinador de Docencia
- L.Q. Esmeralda León Ramos. Coordinador de Difusión Cultural y Extensión

Comité Editorial

- Dr. Carlos Ernesto Lobato García. Editor en Jefe
- Dr. Adib Abiu Silahua Pavón. Gestor Editorial
- Mtra. Claudia Gisela Vázquez Cruz. Editora Asociada. Actuaría
- Mtra. María Hortensia Almaguer Cantú. Editora Asociada. Ciencias de la Computación
- Dr. José Arnold González Garrido. Editor Asociado. Ciencias Farmacéuticas
- Dr. José Luis Benítez Benítez. Editor Asociado. Física
- Mtro. Guillermo Chávez Hernández. Editor Asociado. Geofísica
- Dra. Addy Margarita Bolívar Cimé. Editora Asociada. Matemáticas
- Dra. Nancy Romero Ceronio. Editoria Asociada. Química

UJAT
UNIVERSIDAD JUÁREZ AUTÓNOMA DE TABASCO
"ESTUDIO EN LA DUDA. ACCIÓN EN LA FE"

CONTENIDO

ISSN:2448-4997
https://revistas.ujat.mx/index.php/jobs

Vol. 10 (28), p. 1-9, enero-abril 2024,e-ISSN: 2448 4997
JOURNAL OF BASIC SCIENCES

Pectin Extracted from Orange Peel (*Citrus Sinensis*) to Obtain Bioplastic: Synergistic Effects with Alginate

Hernández-Madrigal, F.[1]; Saavedra-Díaz R. O.[1]; Hernández-Córdova, R.[1*]
[1]División Académica de Ciencias Básicas, Universidad Juárez Autónoma de Tabasco, C.P. 86690 Cunduacán, Tabasco, México.
**roberto.hernandezc@ujat.mx*

Abstract

Pectin, derived from agri-food industry waste, is an almost inexhaustible resource. This study aims to develop a bioplastic from pectin extracted from orange peel, combined with commercial alginate, and to investigate its physicochemical and thermal properties. Pectin was extracted using acid hydrolysis, and its degree of esterification and methoxyl content were determined through titration. The bioplastic film was obtained by ionic cross-linking method. Structural characterization was conducted with Fourier Transform Infrared (FTIR) spectroscopy, while the thermal properties of the pectin and the film were assessed via thermogravimetric analysis (TGA). The results indicated that pectin and alginate exhibited synergistic interactions through miscibility and ionic cross-linking. The bioplastic film demonstrated thermal stability, with a plateau in the range of 130 – 200 °C, indicating that the material possesses suitable properties for thermal processing.

Keywords: *Bioplastic film, Pectin TGA, Methoxy titration*

Recibido: 30 de mayo de 2024, Aceptado: 14 de agosto de 2024, Publicado: 30 de agosto de 2024

1. Introduction

Bioplastics present a sustainable alternative to conventional petroleum-based plastics. Derived from renewable resources, bioplastics offer a promising solution for mitigating ecological damage by being designed to be biodegradable or compostable. Various biomass sources can be utilized to produce bioplastics, including agricultural and agro-industrial residues like orange peel waste. By incorporating these waste materials, agro-industrial activities can become more sustainable, thereby reducing their environmental footprint [1], [2].

Bioplastics have potential applications across diverse industries, including the food, pharmaceutical, and biomedical sectors. In the food industry, they can be utilized for packaging materials, food containers, and single-use items, providing effective protection while reducing plastic waste and promoting a circular economy. In the pharmaceutical and biomedical fields, bioplastics are promising for use in drug delivery systems, tissue engineering scaffolds, and medical implants. Their biocompatibility and biodegradability offer significant advantages, potentially reducing issues related to toxicity and the long-term environmental persistence of traditional plastics [1], [3].

Pectin extracted from orange peel residue presents unique characteristics that position it as an attractive candidate for the bioplastics market. Its abundance, renewability, and biodegradability make it a compelling alternative as a raw material. In the biomedical and pharmaceutical sectors, pectin is valued for its excellent biocompatibility, low toxicity, and gelling properties, which are ideal for drug encapsulation and delivery systems. [4], [5]. Moreover, combining pectin with commercial alginate offers the potential to develop bioplastic films with enhanced properties, including improved mechanical strength, flexibility, and barrier performance [6] – [8].

Combining pectin with alginate is compelling due to their complementary properties. Pectin's excellent gelling abilities and biocompatibility enhance alginate’s superior film-forming capacity and mechanical strength, creating a synergy that improves the structural integrity and flexibility of bioplastic films, thus overcoming the limitations of single-polymer systems. Both materials are abundant and renewable, promoting sustainable development by reducing dependency on fossil-based resources. By tailoring the physicochemical interactions between pectin and alginate, we can optimize barrier properties, making these composite films versatile for packaging and biomedical applications. This innovative approach not only creates more robust and functional bioplastics but also advances the development of environmentally friendly materials.

This study explores the production of bioplastic films using pectin extracted from orange peel (*Citrus sinensis*) residues. The significance of this research lies in its potential to offer sustainable alternatives to conventional plastics, address waste management challenges, and pave the way for eco-friendly applications in the food, pharmaceutical, and biomedical industries. Additionally, alginate is known for producing bioplastics with excellent characteristics. Therefore, this research combines pectin and alginate to evaluate their thermal and structural properties, enhancing hydrogen interactions between the two polymers and potentially improving the film's overall performance.

2. Methodology

2.1. Materials

Orange peel was obtained from a public market in Comalcalco Tabasco, México. Ethanol, sodium hydroxide, sodium chloride, hydrochloric acid, and citric acid were purchased from Meyer. Potassium biphthalate was purchased from Fagalab. Alginate food grade was purchased from MCC.

2.2. Methods

2.2.1. Pectin extraction.

Orange peel was first washed with running water, then cut into pieces and dried in an oven at 80 °C for 24 hours. The dried peel was crushed using a domestic blender and stored for future use. Pectin was extracted by dispersing the crushed orange peel in distilled water at a ratio of 1:25 (g/ml) and heating the mixture to 90 °C for 60 minutes with magnetic stirring at 500 rpm. The pH was maintained at 3.8 using a citric acid solution. After extraction, the mixture was filtered, and pectin was precipitated by adding ethanol at a ratio of 1:4. The precipitated pectin was then filtered and dried in an oven at 80 °C for 24 hours.

2.2.2 Measuring Degree of esterification (DE) and Methoxyl content (DM).

The degree of esterification and methoxyl content were determined via titration. Acid and base solutions were standardized using potassium biphthalate. Sodium hydroxide (NaOH) solutions of 0.1 M and 0.001 M, along with hydrochloric acid (HCl) solution at 0.1 M, were employed. Phenolphthalein served as the indicator. All quantifications were performed in triplicate to ensure accuracy.

2.2.3 Pectin/Alginate film obtaining.

The film was prepared using the solvent evaporation method. First, equal amounts of dry pectin and alginate were weighed. A 2% (w/w) solution of the pectin/alginate mixture in deionized water was prepared at room temperature with continuous magnetic stirring at 300 rpm for 1 hour. The resulting solution was then poured into a Petri dish and dried at 80°C for 18 hours. The film was subsequently immersed in a 2% (w/w) calcium chloride ($CaCl_2$) solution for 4 hours to facilitate ionic cross-linking. Finally, the cross-linked film was dried at 80°C for 12 hours and stored in a sealed bag until needed.

2.2.4 FTIR characterization.

Pectin powder and pectin/alginate films were characterized using a Thermo Scientific Nicolet™ iS™ 50 FTIR spectrometer in Attenuated Total Reflectance (ATR) mode. The analysis was conducted over a wavenumber range of 4000 to 400 cm^{-1} with 60 scans per sample.

2.2.5 TGA characterization.

Pectin powder and pectin/alginate films were characterized using a Setaram Labsys EVO 1110 thermal analyzer. Samples weighing between 5 and 7 mg were analyzed over a temperature range of 34 to 600 °C at a heating rate of 10 °C/min. Argon gas was employed as an inert carrier to maintain an inert environment during the analysis.

3. Results and discussion

3.1. Extraction, yield, and chemical characteristics of the extracted pectin.

Figure 1 displays the pectin precipitate obtained by ethanol precipitation and the resulting pectin/alginate bioplastic film. The precipitate appears as a yellowish, gelatinous substance, suggesting the presence of

residual oils in the extracted pectin. Notably, d-limonene, a key component of orange peel essential oils, is likely contributing to this coloration [9].

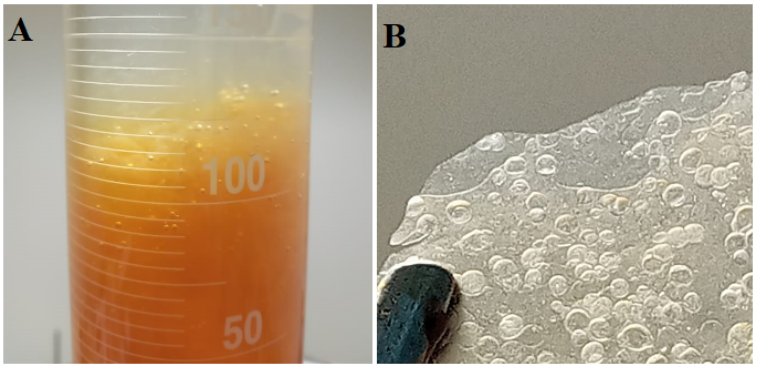


Figure. 1. (A) the pectin precipitate and (B) the pectin/alginate film.

The dry pectin obtained was dark yellow with a citrus aroma. Table 1 presents the yield and chemical characterization of the pectin, including the degree of esterification (DE) and methoxyl content (DM). The yield aligns with the fruit's ripening stage, as ripening induces peel softening, which is linked to pectin depolymerization and solubilization. This process can reduce the molecular mass of pectin by up to 36.18% and decrease pectin content by up to 42.1% after 63 days of storage [10], [11]. Based on the DE and DM values, the pectin is classified as high methoxyl (HMP) and fast gelling, a characteristic attributable to the extraction conditions.

Table 1. Pectin yield, and chemical characteristics. Results are presented in mean ± standard deviation.

Yield	DE	DM
	(%)	
4.95	96.58 ± 0.39	13.81 ± 2.37

3.2. Obtaining pectin/alginate bioplastic film

Figure 1B shows the resulting film, which was translucent, flexible, and resistant to tearing. It adhered well to the Petri dish but could be peeled off easily, without any noticeable defects or fractures. The film exhibited bubbles, a result of the rapid drying process. These fundamental characteristics make it suitable for applications in food packaging and as a protective coating for fruits [7].

3.3. FTIR analysis

Figure 2 displays the FTIR spectra of the extracted pectin and the bioplastic film. The pectin sample exhibits a broad band between 3650 and 3000 cm^{-1}, with a peak at 3348 cm^{-1}, attributed to O-H stretching related to intra- and intermolecular hydrogen bonds in galacturonic acid. A medium-intensity peak is observed at 2932 cm^{-1}, with a shoulder at 2856 cm^{-1}, associated with C-H bending vibrations of the methyl ester group. While this band can be used to identify the degree of esterification (DE) of pectin, it is often obscured by the broad O-H vibrational band [6], [7], [12]. An intense peak at 1719 cm^{-1} is observed, corresponding to the C=O bond vibrations of the methyl ester group. This peak is indicative of high methoxyl pectin (HMP), as intense peaks in this region are characteristic of HMP. In contrast, a less intense peak at 1602 cm^{-1} is associated with the asymmetric carbonyl stretching of the carboxylate ion (COO^-). This lower intensity is

typical of low methoxyl pectin (LMP), which usually exhibits a more pronounced peak in this region. Additionally, an intense peak at 1225 cm^{-1} suggests a high homogalacturonan content in the pectin [12]. In the 1150–935 cm^{-1} region, several peaks characteristic of the pectin fingerprint are observed.

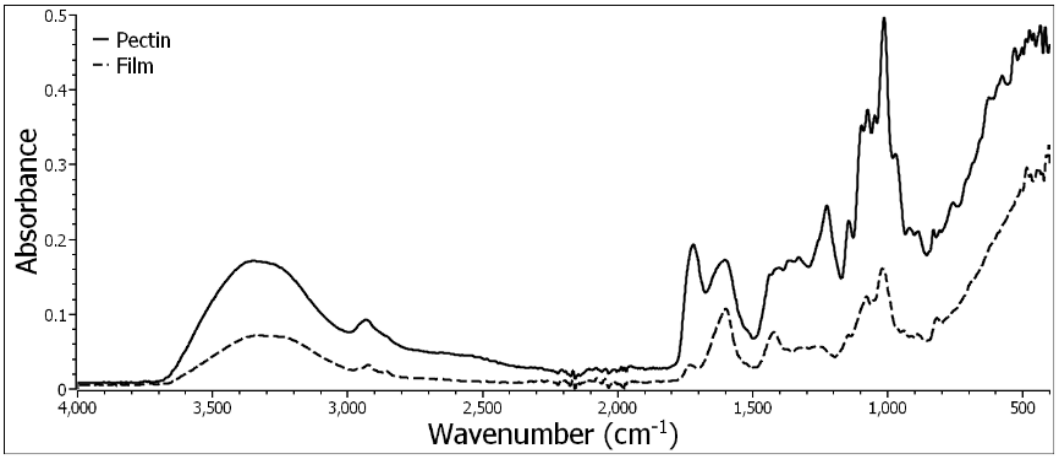


Figure. 2. FTIR of the extracted pectin and the pectin/alginate film.

In the analysis of the film, the O-H bond vibrations exhibited a shift to the right, with a maximum at 3345 cm^{-1}, suggesting enhanced hydrogen bonding interactions between pectin and alginate. Additionally, a rightward shift was observed for the peaks corresponding to C-H vibrations, now occurring at 2924 cm^{-1} and 2852 cm^{-1}, respectively. The peak associated with the C=O bond vibrations of the methyl ester group decreased in intensity and shifted to the left at 1732 cm^{-1}. An intense peak at 1599 cm^{-1} and a medium-intensity peak at 1421 cm^{-1} were identified, corresponding to the asymmetric and symmetric vibrations of the carboxylate ion (COO^-), indicating ionic cross-linking with Ca^{2+} [13].

3.4. Thermal analysis

Figure 3 presents the TGA test results for the pectin and bioplastic film. Generally, the decomposition of these materials is associated with three main events: moisture loss, depolymerization, and the decomposition of polysaccharides, followed by ash formation. Specifically, pectin decomposes in three primary stages, while the film exhibits four distinct decomposition stages. A detailed analysis of these decomposition stages is provided in Tables 2 and 3 for the pectin and film, respectively. The decomposition temperature (Td) for the film was determined as the intersection point marking the change in slope on the TGA curve, with the corresponding mass loss quantified at this temperature. Since the TGA curve for pectin did not exhibit a stable zone after moisture loss, the decomposition temperature (Td) was determined using the onset from the DTG curve. The Td for pectin was found to be 187.6 °C, with a mass loss of 12.6%. Conversely, the Td for the film was 209.9 °C, accompanied by a mass loss of 9.6%. The TGA of the pectin/alginate film demonstrated a plateau of thermal stability from 150 °C to over 200 °C. It has been reported that this type of film has a melting temperature around 133 °C [7], [14]. This result suggests that our material possesses a broad range of thermal processability, making it suitable for various thermal processing applications.

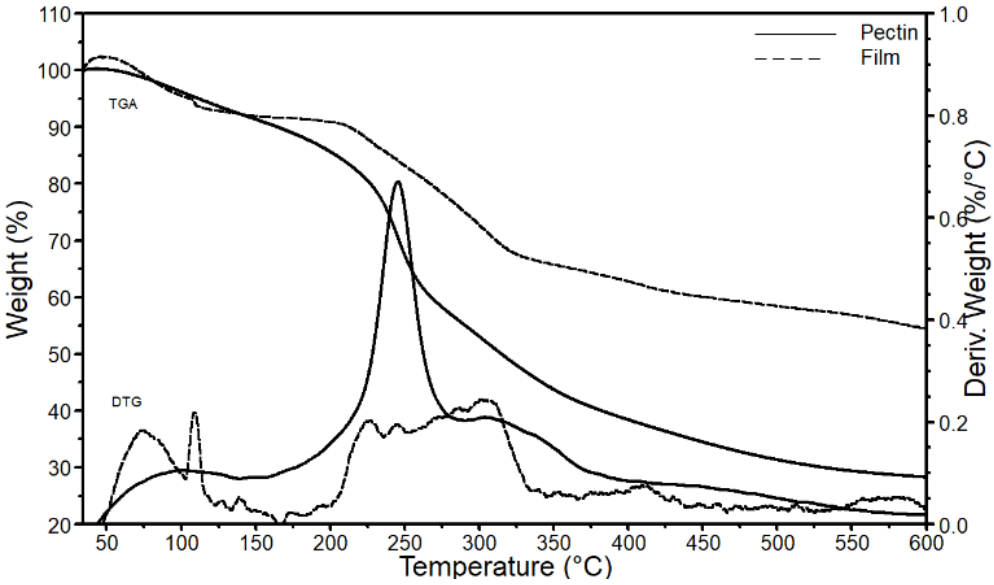


Figure. 3. Thermogravimetric analysis of the extracted pectin and pectin/alginate film.

The peak temperature (Tp) for pectin was observed at 245.0 °C, with a maximum decomposition rate (Vmax) of 0.69 %/°C. This sharp peak in the DTG curve (Figure 3) suggests that the extracted pectin has a homogeneous composition. Conversely, the pectin/alginate film exhibited a broad band during the polysaccharide decomposition stage, with three distinct peaks at 227.1 °C, 244.7 °C, and 301.1 °C, and a Vmax of 0.25 %/°C at the highest temperature peak. This broad band on the DTG curve indicates successful synergy between the pectin and alginate polymers, enhancing their resistance to thermal degradation during the polysaccharide decomposition stage. The increased stability can be attributed to the formation of additional hydrogen bonds between pectin and alginate and the ionic cross-linking effect between the COO^- groups of both polymers with Ca^{2+}, as confirmed by the FTIR analysis.

Table 2. Pectin thermal decomposition analysis.

Interval	Weight loss	Stage
(°C)	(%)	
35 – 198.5	14.1	Moisture evaporation
198.5 – 375.1	45.2	Pectin decomposition
375.1 – 600	12.4	Ash forming

At the end of the thermal decomposition process, residue amounts of 28.3% for pectin and 54.6% for the film were recorded. The increased ash content in the film correlates with enhanced thermal stability, attributable to the interactions between the polymers and the presence of Ca^{2+} ions. This difference further highlights the stabilizing effect of ionic cross-linking in the composite material.

Table 3. Pectin/Alginate film thermal decomposition analysis.

Interval	Weight loss	Stage
(°C)	(%)	
35 – 204.2	9.2	Moisture evaporation
204.2 – 331.6	23.8	Pectin and alginate two
331.6 – 429.7	6.0	stages of decomposition
429.7 – 600	6.4	Ash forming

4. Conclusions

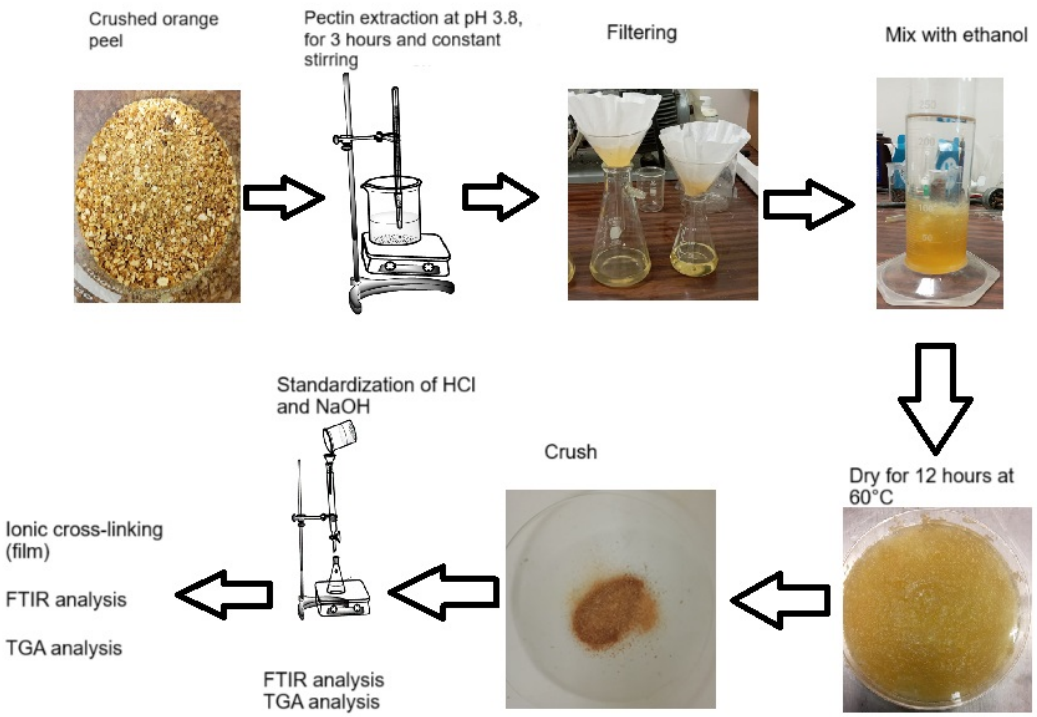
We successfully obtained a fast-gelling, high methoxyl pectin (HMP) with excellent properties for bioplastic production. The combination of the extracted pectin with commercial alginate enhanced hydrogen bond interactions between the two polymers. The ionic cross-linking method facilitated interactions between the COO^- groups of both polymers and Ca^{2+} ions, contributing to increased thermal stability. The enhanced hydrogen bonding and the interactions between COO^- and Ca^{2+} resulted in a pectin/alginate film with superior thermal properties, making it a promising candidate for bioplastic production through extrusion or thermal molding.

Our findings demonstrate the potential to create high-quality bioplastics from pectin sourced from agri-food industry waste, effectively utilizing alginate to improve performance. This approach not only supports sustainability but also paves the way for innovative material applications in bioplastic development.

5. Acknowledgments

The authors express their gratitude to the Centro de Investigación de Ciencia y Tecnología Aplicada de Tabasco (CICTAT) at the Universidad Juárez Autónoma de Tabasco for their invaluable support in conducting the FTIR and TGA analyses, made possible through project INFR-2016-01-269701.

6. Graphical abstract



7. References

[1] I. S. Sidek, S. F. S. Draman, S. R. S. Abdullah, and N. Anuar, "Current Development on Bioplastics and Its Future Prospects: an Introductory Review," INWASCON Technology Magazine, vol. 1, pp. 03–08, 2019, doi: 10.26480/itechmag.01.2019.03.08.
[2] G. Bhagwat et al., "Benchmarking Bioplastics: A Natural Step Towards a Sustainable Future," Journal Polymer Environ, vol. 28, no. 12, pp. 3055–3075, 2020, doi: 10.1007/s10924-020-01830-8.
[3] C. Mellinas, M. Ramos, A. Jiménez, and M. C. Garrigós, "Recent trends in the use of pectin from agrowaste residues as a natural based biopolymer for food packaging applications," Materials, vol. 13, no. 3, 2020, doi: 10.3390/ma13030673.
[4] Li, D. Q., Li, J., Dong, H. L., Li, X., Zhang, J. Q., Ramaswamy, S., and Xu, F. "Pectin in biomedical and drug delivery applications: A review," International Journal of Biological Macromolecules, vol. 185, no. March, pp. 49–65, 2021, doi: 10.1016/j.ijbiomac.2021.06.088.
[5] C. Wang, W. Y. Qiu, T. T. Chen, and J. K. Yan, "Effects of structural and conformational characteristics of citrus pectin on its functional properties," Food Chem, vol. 339, no. September 2020, p. 128064, 2021, doi: 10.1016/j.foodchem.2020.128064.
[6] Makaremi, M., Yousefi, H., Cavallaro, G., Lazzara, G., Goh, C. B. S., Lee, S. M., ... and Pasbakhsh, P. Safely dissolvable and healable active packaging films based on alginate and pectin. Polymers (Basel), vol. 11, no. 10, pp. 1–18, 2019, doi: 10.3390/polym11101594.
[7] S. S. N. Chakravartula, M. Soccio, N. Lotti, F. Balestra, M. Dalla Rosa, and V. Siracusa, "Characterization of composite edible films based on pectin/alginate/whey protein concentrate," Materials, vol. 12, no. 15, pp. 1–19, 2019, doi: 10.3390/ma12152454.
[8] M. M. Saldívar Guevara, V. Saucedo-Rivalcoba, J. L. Rivera-Armenta, and L. I. Elvira-Torales, "Evaluation of a Cross-Linking Agent in the Preparation of Films Based on Chitosan and Pectin for Food Packaging Applications," Cellulose Chemistry and Technology, vol. 56, no. 9–10, pp. 1061–1070, 2022, doi: 10.35812/CelluloseChemTechnol.2022.56.94.
[9] A. Kumar Tiwari, S. Nath Saha, V. Prasad Yadav, U. Kumar Upadhyay, D. Katiyar, and T. Mishra, "Extraction and Characterization of Pectin from Orange Peels," International Journal of Biotechnology and Biochemistry, vol. 13, no. 1, pp. 39–47, 2017, [Online]. Available: http://www.ripublication.com
[10] Deng, L. Z., Pan, Z., Zhang, Q., Liu, Z. L., Zhang, Y., Meng, J. S., ... and Xiao, H. W. "Effects of ripening stage on physicochemical properties, drying kinetics, pectin polysaccharides contents and nanostructure of apricots," Carbohydr Polym, vol. 222, no. February, p. 114980, 2019, doi: 10.1016/j.carbpol.2019.114980.
[11] Frempong, K. E. B., Chen, Y., Wang, Z., Xu, J., Xu, X., Cui, W., ... and Lin, X. "Study on textural changes and pectin degradation of tarocco blood Orange during storage," International Journal Food Properties, vol. 25, no. 1, pp. 344–358, 2022, doi: 10.1080/10942912.2022.2032736.
[12] E. E. Santos, R. C. Amaro, C. C. C. Bustamante, M. H. A. Guerra, L. C. Soares, and R. E. S. Froes, "Extraction of pectin from agroindustrial residue with an ecofriendly solvent: use of FTIR and chemometrics to differentiate pectins according to degree of methyl esterification," Food Hydrocoll, vol. 107, no. December 2019, 2020, doi: 10.1016/j.foodhyd.2020.105921.
[13] M. A. Patel, M. H. H. AbouGhaly, J. V. Schryer-Praga, and K. Chadwick, "The effect of ionotropic gelation residence time on alginate cross-linking and properties," Carbohydr Polym, vol. 155, pp. 362–371, 2017, doi: 10.1016/j.carbpol.2016.08.095.

[14] Amante, C., Andretto, V., Rosso, A., Augusti, G., Marzocco, S., Lollo, G., and Del Gaudio, P. "Alginate-pectin microparticles loaded with nanoemulsions as nanocomposites for wound healing," Drug Deliv Transl Res, vol. 13, no. 5, pp. 1343–1357, 2023, doi: 10.1007/s13346-022-01257-9.