

Natural Deep Eutectic Solvent (NADES) as Plasticizer for Bioplastic Film Fabrication. A Comparative Study

Shiou Xuan Tan¹, Andri Andriyana^{2*}, Steven Lim³, Hwai Chyuan Ong⁴, Yean Ling Pang⁵, Gek Cheng Ngoh⁶

^{1,2} Department of Mechanical Engineering, Faculty of Engineering, Universiti Malaya, Kuala Lumpur 50603, Malaysia

^{3,5} Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Kajang 43000, Malaysia

⁴ Future Technology Research Center, National Yunlin University of Science and Technology, Douliou 64002, Taiwan

⁶ Centre of Separation Science and Technology, Department of Chemical Engineering, Faculty of Engineering, Universiti Malaya, Kuala Lumpur 50603, Malaysia

*Corresponding author

doi: <https://doi.org/10.21467/proceedings.141.23>

ABSTRACT

Incorporation of chitosan into the bioplastic film could improve its mechanical properties. However, aqueous acidic solution is required to dissolve the chitosan. The aim of the present work was to explore the potential use of acidic NADES as the plasticizer as well as a solvent for chitosan without the addition of aqueous acidic solution. The film-forming solution consisted of sago starch as the matrix and chitosan as the filler was prepared by solution casting and evaporation method in the presence of acidic NADES. Acidic NADES was obtained by mixing choline chloride (ChCl) and lactic acid (LA) as the hydrogen bond acceptor and hydrogen bond donor, respectively. The mechanical properties and water uptake ability of chitosan-reinforced starch-based bioplastic films plasticized with acidic NADES were compared with the bioplastic films plasticized with conventional plasticizer, glycerol in the absence and presence of acetic acid solution. The results revealed that acidic NADES was capable of plasticizing the starch and dissolving the chitosan. Bioplastic film plasticized with acidic NADES achieved higher tensile strength and lower water uptake than the bioplastic film plasticized with glycerol in the presence of acetic acid solution. The interaction between chitosan and acidic NADES was confirmed by Fourier-transform infrared spectroscopy (FTIR). FTIR results exhibited that the amide II band of chitosan in the ChCl/LA film had shifted, and its intensity had decreased to almost undetectable.

Keywords: Bioplastic, choline chloride, chitosan

1 Introduction

Starch is an abundant, inexpensive, and natural renewable raw material [1]. Brittleness and poor film forming capacity of native starch limit its application in bioplastic film synthesis. Plasticization is often adopted to overcome these shortcomings [2]. Water and glycerol are the most common plasticizers for starch. However, high volatility of water is not suggested as the film produced will be brittle [3]. On the other hand, glycerol is susceptible to migration in starch materials, causing starch retrogradation after prolong storage time [4]. Ionic liquid is emerging as a new plasticizer in bioplastic film synthesis to its dissolving ability. Nonetheless, time consuming synthesis and purification have incurred high production cost. Moreover, its green character is disputable from the aspect of its toxicity [5]. It is sometimes even more toxic than some organic solvents [6].



Considering the limitations of the aforementioned plasticizers, natural deep eutectic solvent (NADES) is a potential candidate as green plasticizer in bioplastic film synthesis. NADES has high dissolution ability as water and glycerol [5]. As compared with ionic liquid, NADES is non-toxic and cheaper to be prepared. It can be prepared from natural and easily available compounds in a simple and convenient way via thermal mixing [5, 6]. DES is formed by mixing hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) [7]. Choline chloride (ChCl) is the commonly applied HBA as it is easily available, cheap, biodegradable (over 93% within 14 days) [5].

In addition to plasticization, addition of filler such as chitosan could enhance the mechanical properties of starch-based bioplastic film. However, chitosan only can be dissolved in aqueous acidic solution with pH <6.3 due to the conversion of glucosamine units into soluble protonated form $R-NH_3^+$ [8, 9]. In view of this, acidic NADES such as choline chloride/lactic acid (ChCl/LA) could act as a plasticizing agent and a solvent for chitosan as well.

To present, there is no report available on the fabrication of chitosan-reinforced starch-based bioplastic film using acidic NADES as the plasticizer. Herein, the mechanical properties of the bioplastic films plasticized with ChCl/LA were compared to the bioplastic film plasticized with the conventional plasticizer, glycerol in the absence and presence of acetic acid solution. Plasticization efficiency of NADES in the starch-based bioplastic films was investigated through tensile test, FTIR analysis and water uptake test.

2 Materials and Methods

2.1 Materials

Starch was extracted from sago pith waste (SPW) as matrix of bioplastic film. SPW was provided by Craun Research Sdn. Bhd., Kuching, Malaysia. Choline chloride ($\geq 98\%$ purity) and glycerol ($\geq 99\%$ purity) were procured from Sigma Aldrich. Lactic acid (88% purity) was supplied by R&M Chemicals whereas acetic acid (100% purity) was procured from Merck.

2.2 Preparation of natural deep eutectic solvent (NADES)

ChCl and lactic acid (LA) were utilized as the HBA and HBD, respectively. ChCl and LA were mixed at the molar ratio of 1:1. Mixtures were heated in 80°C water bath under stirring until a homogeneous and pellucid liquid was obtained. NADES was allowed to cool to room temperature for overnight before use [10].

2.3 Preparation of bioplastic film

The chitosan-reinforced starch-based bioplastic film was fabricated as described by Agustin et al. [11] with slight modification. 100 mL of distilled water was mixed with 5.0 g of sago starch and 0.25 g of chitosan to produce starch solution. It was homogenized at 250 rpm and heated at 60 °C for 15 min. 40 wt.% of NADES (with respect to dried starch) [12] was added into the starch solution and heated at 70°C until it was gelatinized. 15.0 g of starch mixture was placed in a square container (10 cm × 10 cm) and dried in a heating oven at 60°C for 24 h. The ChCl/LA film was sealed in a plastic bag and was stored in a desiccator after drying. Glycerol as the conventional plasticizer was used for the comparison purpose. The chitosan was dissolved in 100 mL of 1 vol% acetic acid solution (Gly/AA film) and distilled water (Gly film) in the presence of glycerol, respectively.

2.4 Characterization of prepared bioplastic films

2.4.1 Tensile test

A bioplastic film with dimension of 7 cm × 1 cm was subjected to tensile test using Universal Testing Machine (Autograph AG-X, Shimadzu, Japan) equipped with 500 N load cell and interfaced with computer operating Trapezium software according to ASTM D882-02 [13]. Grip separation and crosshead speed used were 30 mm and 5 mm/min. Three measurements were taken at three random places of each film and the average value was reported.

2.4.2 Fourier-transform infrared (FTIR) analysis

The functional groups and chemical bonds of the films were measured using FTIR spectrometer (Perkin Elmer, model Spectrum 400) in attenuated total reflectance (ATR) mode. Measurements were taken in a wavenumber range of 4000–550 cm⁻¹ with 32 scans at a resolution of 4 cm⁻¹.

2.4.3 Water uptake test

A bioplastic film with dimension of 1.5 cm × 2 cm was dried in the oven at 50 °C for 24 h and weighed as W_o . The bioplastic film was immersed in distilled water for 10 s at room temperature and reweighed as W_f . Water uptake was calculated according to Eq. (1). Average reading was taken from triplicate runs [14].

$$\text{Water uptake (\%)} = \frac{W_f - W_o}{W_o} \times 100 \quad (1)$$

3 Results and Discussion

3.1 Visual appearance of bioplastic films

It is noticed from Figure 1 that all the three films were in semi-transparent brownish colour without any cracks. In general, all the films exhibited good handling properties and were easily separated from their containers. Both ChCl/LA and Gly/AA films showed smooth and homogeneous with thickness of 0.11 ± 0.01 mm but Gly film was not homogeneous with insoluble particles observed. The thickness of Gly film was 0.13 ± 0.01 mm.

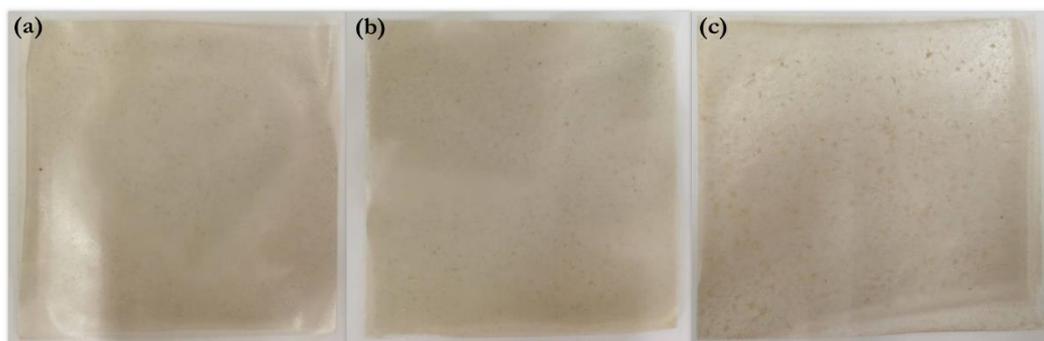


Figure 1: Appearance of bioplastic films with (a) ChCl/LA, (b) Gly/AA and (c) Gly as plasticizers.

3.2 Fourier transform infrared spectroscopy (FTIR)

Figure 2 shows the FTIR spectra of chitosan powder, ChCl/LA, Gly/AA and Gly films. Characteristic peaks of chitosan powder at 1647 cm⁻¹ and 1571 cm⁻¹ were attributed to amide I (C=O stretching) and amide II (C–N stretching and C–N–H bending vibrations), respectively [15]. In the ChCl/LA film, the amide II band had shifted, and its intensity had decreased to almost undetectable. This observation could be related to the ionic interaction between protonated amino groups of chitosan and carboxylate (–COO)

ions of lactic acid [9, 10]. On the other hand, the amide II band was remained noticeable at 1569 cm^{-1} in the Gly/AA film. This finding could possibly reveal that chitosan dissolved better in ChCl/LA. Although both Gly and Gly/AA films depicted similar spectrum, some minor differences were observed. Besides shifting of the absorption bands, one new peak was observed at 1015 cm^{-1} in the Gly/AA film. This phenomenon could be the results of the interaction between cation of the acetic acid and the nitrogen atom of the amine group [16].

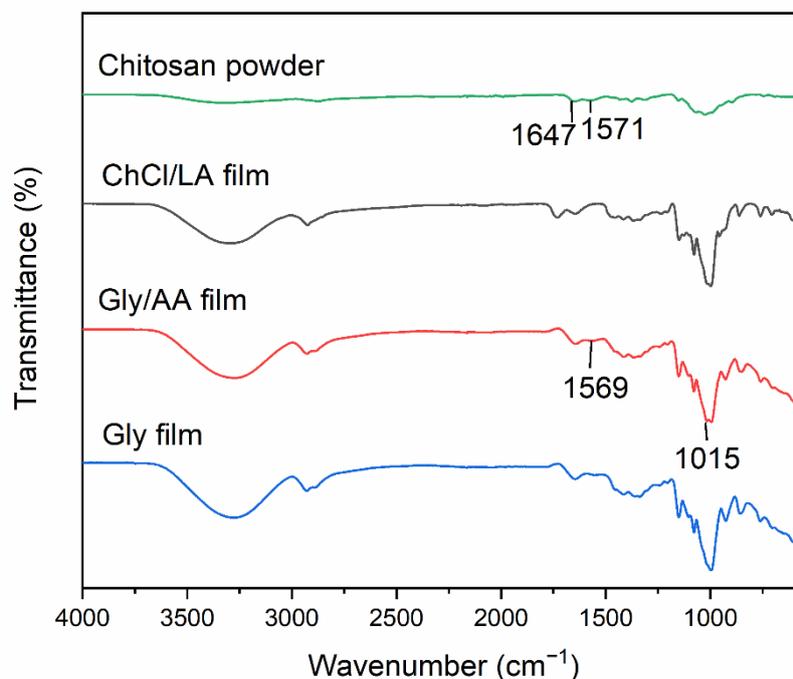


Figure 2: FTIR spectra of chitosan powder, ChCl/LA, Gly/AA and Gly films.

3.3 Mechanical properties of bioplastic films

It is observed from Figure 3 that the tensile strength of films was in the decreasing order of ChCl/LA > Gly/AA > Gly and elongation at break was in the decreasing order of Gly/AA > Gly > ChCl/LA. Film with ChCl/LA achieved the highest tensile strength of 4.38 MPa and the lowest elongation at break of 16.74% among all the films. These could be attributed to more available functional groups in the eutectic mixtures to hydrogen bond formation with starch chains [17]. Stronger O-N.H hydrogen bonds could be formed between the N^+ of the ChCl and the -OH of starch. Moreover, O-H...Cl hydrogen bonds could be also formed between the Cl^- of ChCl and the -OH of starch [1, 18]. In the present of acetic acid, tensile strength of 2.77 MPa and elongation at break of 25.93% were attained by Gly/AA film. On the hand, chitosan could not dissolve completely in the absence of acetic acid solution. Therefore, the lowest tensile strength of 0.58 MPa was observed for Gly film. Although both the glycerol containing films (Gly/AA and Gly) had higher elongation at break than ChCl/LA containing films, its higher evaporation than NADES would result in stiffening of the film which is unfavourable in many applications [19].

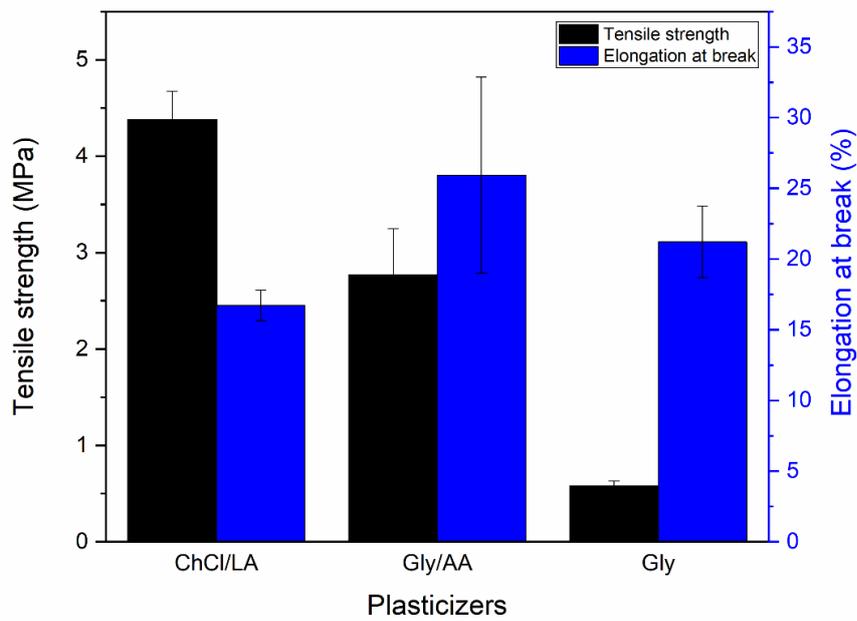


Figure 3: Mechanical properties of bioplastic films with different plasticizers.

3.4 Water uptake

It was noticed from Figure 4 that Gly/AA had the highest water uptake percentage of 54.1% followed by ChCl/LA (39.9%) and Gly (35.3%). The highest water uptake by Gly/AA film could be related to its highest flexibility among the three bioplastic films. An increase in the intramolecular distance between the starch and chitosan chains could lead to an increase in the water uptake [9]. For ChCl/LA and Gly films, there was a minor difference in the water uptake between them. Glycerol has three -OH groups which can interact with water molecular to form hydrogen bonds whereas ChCl/LA is a highly hydrophilic plasticizer in which both plasticizers favour the water uptake [9]. Slightly higher water uptake in the ChCl/LA film than the Gly film could be possibly due to higher hydrophilicity of ChCl/LA than the glycerol. Higher water uptake is preferable as higher water absorption attracts the microorganisms to attack the bioplastic and thus improving the biodegradability properties of bioplastic [20].

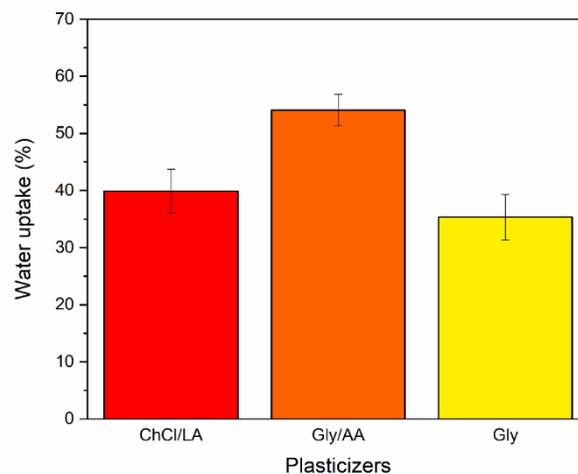


Figure 4: Water uptake percentages of bioplastic films with different plasticizers.

4 Conclusions

Chitosan-reinforced starch-based bioplastic films plasticized with acidic NADES was successfully prepared via solution casting and evaporation method. The preliminary results of the present work revealed that ChCl/LA as the acidic NADES could be the plasticizer for starch-based bioplastic film as well as a solvent for chitosan. This finding proved that ChCl/LA could serve the same function as acetic acid. From the tensile test results, ChCl/LA film achieved the highest tensile strength of 4.38 MPa with the lowest elongation at break of 16.74%. In view of the low flexibility of ChCl/LA film, different formulations of the chitosan and plasticizer loadings could be conducted to improve the flexibility of the film. Future studies could focus the mechanical properties of chitosan-reinforced starch-based bioplastic film plasticized with different acidic NADES.

5 Declarations

5.1 Funding source

The research was funded by Universiti Malaya, Kuala Lumpur under RU Grant (GPF059A-2020) and Universiti Tunku Abdul Rahman Research Grant (UTARRF/6200-W83).

5.2 Competing Interests

The authors declare no conflict of interest.

5.3 Publisher's Note

AIJR remains neutral with regard to jurisdiction claims in published maps and institutional affiliations.

References

- [1] L. Zeng *et al.*, "Structure and functionality of cassava starch in different deep eutectic solvents/water mixtures: A comparative study," *Industrial Crops and Products*, vol. 177, p. 114453, 2022, doi: 10.1016/j.indcrop.2021.114453.
- [2] A. Ashok, C. Rejeesh, and R. Renjith, "Biodegradable polymers for sustainable packaging applications: a review," *International Journal of Bionics and Biomaterials*, vol. 2, no. 2, pp. 1-11, 2016. Accessed online on 15 July 2022 at https://www.researchgate.net/profile/Rejeesh-C-R-2/publication/318531449_Biodegradable_Polymers_for_Sustainable_Packaging_Applications_A_Review/links/59888629aca27266ada4a10e/Biodegradable-Polymers-for-Sustainable-Packaging-Applications-A-Review.pdf.
- [3] Y. Chan, S. Phang, T. Tee, T. Lee, and T. Soo, "Preliminary Study of Mechanical Properties in Thermoplastic Starch (TPS)/Coffee-Waste-Derived Fillers Composites," presented at the Engineering Undergraduate Research Catalyst Conference (EURECA), Sunway, Selangor, Malaysia, 1-2 July, 2015. Accessed online on 15 July 2022 at https://expert.taylors.edu.my/file/remis/publication/104770_1817_1.pdf.
- [4] M. Zdanowicz, R. Jędrzejewski, and R. Pilawka, "Deep eutectic solvents as simultaneous plasticizing and crosslinking agents for starch," *International Journal of Biological Macromolecules*, vol. 129, pp. 1040-1046, 2019, doi: 10.1016/j.ijbiomac.2019.02.103.
- [5] M. Zdanowicz, K. Wilpiszewska, and T. Szychaj, "Deep eutectic solvents for polysaccharides processing. A review," *Carbohydrate Polymers*, vol. 200, pp. 361-380, 2018, doi: 10.1016/j.carbpol.2018.07.078.
- [6] S. Khodaverdian, B. Dabirmanesh, A. Heydari, E. Dashtban-Moghadam, K. Khajeh, and F. Ghazi, "Activity, stability and structure of laccase in betaine based natural deep eutectic solvents," *International Journal of Biological Macromolecules*, vol. 107, pp. 2574-2579, 2018, doi: 10.1016/j.ijbiomac.2017.10.144.
- [7] Y. T. Tan, G. C. Ngoh, and A. S. M. Chua, "Effect of functional groups in acid constituent of deep eutectic solvent for extraction of reactive lignin," *Bioresource Technology*, vol. 281, pp. 359-366, 2019, doi: 10.1016/j.biortech.2019.02.010.
- [8] M. R. Kumar, R. A. Muzzarelli, C. Muzzarelli, H. Sashiwa, and A. Domb, "Chitosan chemistry and pharmaceutical perspectives," *Chemical reviews*, vol. 104, no. 12, pp. 6017-6084, 2004, doi: 10.1021/cr030441b.
- [9] E. Jakubowska, M. Gierszewska, J. Nowaczyk, and E. Olewnik-Kruszkowska, "The role of a deep eutectic solvent in changes of physicochemical and antioxidative properties of chitosan-based films," *Carbohydrate Polymers*, p. 117527, 2021, doi: 10.1016/j.carbpol.2020.117527.
- [10] A. C. Galvis-Sánchez, M. C. R. Castro, K. Biernacki, M. P. Gonçalves, and H. K. S. Souza, "Natural deep eutectic solvents as green plasticizers for chitosan thermoplastic production with controlled/desired mechanical and barrier properties," *Food Hydrocolloids*, Article vol. 82, pp. 478-489, 2018, doi: 10.1016/j.foodhyd.2018.04.026.

-
- [11] M. B. Agustin, B. Ahmmad, S. M. M. Alonzo, and F. M. Patriana, "Bioplastic based on starch and cellulose nanocrystals from rice straw," *Journal of Reinforced Plastics and Composites*, vol. 33, no. 24, pp. 2205-2213, 2014, doi: 10.1177/0731684414558325.
- [12] R. F. Santana et al., "Characterization of starch-based bioplastics from jackfruit seed plasticized with glycerol," *Journal of Food Science and Technology*, vol. 55, no. 1, pp. 278-286, Jan 2018, doi: 10.1007/s13197-017-2936-6.
- [13] ASTM, "Standard test method for tensile properties of thin plastic sheeting-D882-02," *Annual book of ASTM standards, American Society for Testing and Materials, Philadelphia*, pp. 1-9, 2002. Accessed online on 15 July 2022 at <https://webstore.ansi.org/Standards/ASTM/ASTMD88202#:~:text=ASTM%20D882-02%20Standard%20Test%20Method%20for%20Tensile%20Properties,%28less%20than%201.0%20mm%20%280.04%20in.%29%20in%20thickness%29>.
- [14] N. D. Masdar, R. Yusof, and N. A. Ramzani, "EFFECT OF DEEP EUTECTIC SOLVENT ON TENSILE PROPERTIES AND BIODEGRADATION OF PECTIN WITH EGG SHELL BIOPLASTIC," *Malaysian Journal of Analytical Sciences*, vol. 26, no. 1, pp. 58-69, 2022. Accessed online on 15 July 2022 at https://mjas.analis.com.my/mjas/v26_n1/pdf/Daina_26_1_7.pdf
- [15] P. F. Pereira and C. T. Andrade, "Optimized pH-responsive film based on a eutectic mixture-plasticized chitosan," *Carbohydrate Polymers*, vol. 165, pp. 238-246, 2017, doi: 10.1016/j.carbpol.2017.02.047.
- [16] S. R. Majid and A. K. Arof, "Proton-conducting polymer electrolyte films based on chitosan acetate complexed with NH₄NO₃ salt," *Physica B: Condensed Matter*, vol. 355, no. 1-4, pp. 78-82, 2005, doi: 10.1016/j.physb.2004.10.025.
- [17] M. Zdanowicz, "Starch treatment with deep eutectic solvents, ionic liquids and glycerol. A comparative study," *Carbohydrate Polymers*, Article vol. 229, 2020, Art no. 115574, doi: 10.1016/j.carbpol.2019.115574.
- [18] H. Xu, W. Pan, R. Wang, D. Zhang, and C. Liu, "Understanding the mechanism of cellulose dissolution in 1-butyl-3-methylimidazolium chloride ionic liquid via quantum chemistry calculations and molecular dynamics simulations," *Journal of computer-aided molecular design*, vol. 26, no. 3, pp. 329-337, 2012, doi: 10.1007/s10822-012-9559-9.
- [19] J. A. Sirviö, M. Visanko, J. Ukkola, and H. Liimatainen, "Effect of plasticizers on the mechanical and thermomechanical properties of cellulose-based biocomposite films," *Industrial Crops and Products*, vol. 122, pp. 513-521, 2018, doi: 10.1016/j.indcrop.2018.06.039.
- [20] Y. Kusumastuti, N. R. E. Putri, D. Timotius, and M. W. Syabani, "Effect of chitosan addition on the properties of low-density polyethylene blend as potential bioplastic," *Heliyon*, vol. 6, no. 11, p. e05280, 2020, doi: 10.1016/j.heliyon.2020.e05280.