https://doi.org/10.24867/GRID-2022-p48 Original scientific paper

THE INVESTIGATION OF EDIBLE PACKAGING FILMS BASED ON PULLULAN AND ALGINATE

Nevena Vukić [1], Tamara Erceg [2], Miroslav Hadnađev [3]
[1] University of Kragujevac, Faculty of Technical Sciences, Čačak, Serbia
[2] University of Novi Sad, Faculty of Technology Novi Sad, Novi Sad, Serbia
[3] University of Novi Sad, Institute of Food Technology in Novi Sad, Novi Sad, Serbia

Abstract: *The packaging industry is highly dependent on fossil resources and have serious environmental drawbacks. The largest part of the total volume of plastic waste is generated from food packaging, so new packaging strategies with green materials are required. Using the edible packaging films which are renewable, biodegradable and versatile, can reduce the amount of plastic waste. Also, there is an increasing demand of higher quality foods and a growing interest from consumers for minimally processed fresh-like foods with an extended shelf life. Edible films can be effective barriers which prevent unwanted mass transfers in foods. They can be green alternative to synthetic petroleum-based polymer packaging materials and nowadays this topic is a fast-growing area. Sodium alginate as a natural polysaccharide can be used for edible films with excellent properties such as transparency. But, sodium alginate practical applications in food packaging are limited as single-component because of poor mechanical and barrier properties. At the same time, pullulan is an extracellular and water-soluble microbial polysaccharide with good film-formation properties. The packaging materials made from pullulan and alginate may be better candidates for edible packaging films. The objective of this study was to formulate pullulan and sodium alginate based edible films for food packaging. For that purpose a series of pullulan/alginate films with different ratios were prepared. To improve film flexibility and processability, glycerol was added as plasticizers in the film formulation. Designed films were solvent cast from aqueous polymer solution. Understanding the film-forming mechanism during the drying process is crucial to predict properties of the obtained films, so rheological properties of prepared solutions were investigated. Formulated films have the potential to be used as inner primary packaging and can be manufactured by preparing a film-forming composition and enclosing a food product with the film. Using this kind of packaging material, no waste is generated contributing to the circular economy.*

Key words: packaging, edible film, rheology, alginate, pullulan

1. INTRODUCTION

The biodegradable and eco-friendliness of packaging materials are desirable benefits associated with their use, primarily in the food industry. Also, there is constantly need to extend shelf life of food products, which is these days specially enlarged. This can be achieved by enriching of packaging food materials with active agents, which decrease the growth of pathogens in food. Wrapping of food by film with antimicrobials which slowly release from the packaging material and dissolve onto the surface of the food through direct contact, results in significantly greater shelf life of packaged food (Erceg et al., 2022). Another possibility of achieving the mentioned requirements is the application of edible films as food packaging materials. Edible films and coatings are promising for delaying quality deterioration of food products and they function as natural preservation and a safe protection for food (Giancone et al., 2008; Apriliyani, Rahayu & Thohari, 2022). They also improve the gas and moisture barriers, mechanical properties, sensory perceptions, and microbial protection and prolong the shelf life of various products, such as foods (Janjarasskul & Krochta, 2010).

Edible films and coatings are made from edible biopolymers and food-grade additives (Jung, 2014). Pullulan films have properties which make them an ideal material for edible films and coatings. Despite the many potential applications of pullulan, extensive use of this polymer is hampered by its high cost (Tong, Xiao & Lim, 2008). One of the possibilities to reduce the cost of pullulan-based films is to blend them with other compatible biopolymers, such as sodium alginate, which films have excellent properties such as transparency, but poor mechanical and barrier properties.

Thin layers on edible products are usually applied as a liquid with varying viscosity on the surface of fresh and processed foods by spraying, spreading and dipping technique (Apriliyani, Rahayu & Thohari, 2022). The properties of the produced edible films and coatings are in correlation with a rheological properties of film-forming solution. The rheological properties describe the flow behavior of film-forming solution, hence becomes a crucial property because it influences the spreading ability, thickness, uniformity of casting layer and consequently affect the performance of the film (Silva-Weiss et al., 2013; Chen, Kuo & Lai, 2009).

The aim of this research was to investigate rheological properties of film-forming pullulan/sodium alginate solutions. For that reason, solutions with different ratios of pullulan and alginate were prepared by a casting method and dried, yielded uniform coherent films. Flow properties of film-forming solutions are important to identify the most appropriate coating system and optimize operating conditions (Ma et al., 2017). Therefore, it was necessary to study the rheological properties of the prepared pullulan/alginate solutions, specially because the flow behavior of film-forming solutions could affect the mechanical properties, and the application and processing design.

2. EXPERIMENTAL SECTION

2.1 Materials

Pullulan with a molecular weight of 574.570 g/mol was supplied from Avena Lab (Serbia). Alginic acid sodium salt was obtained from Alfa Aesar (USA). Structural formulas of pullulan and alginic acid are shown in Figure 1a and Figure 1b, respectively. Glycerol, which was used as a plastificator was purchased from ZORKA Pharma (Serbia).

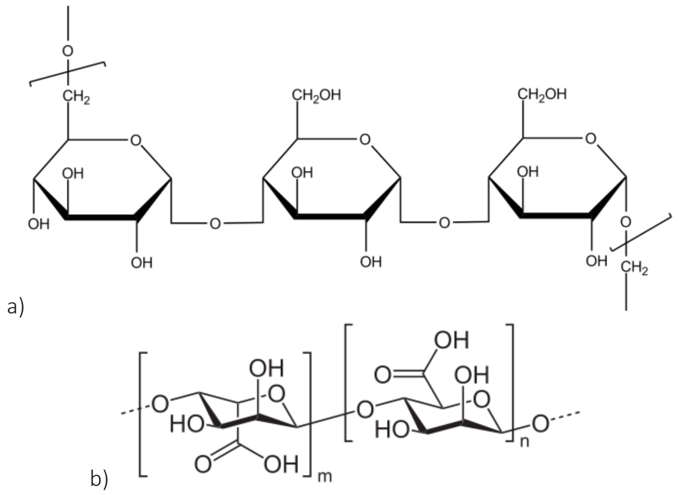


Figure 1: Structural formula of pullulan (a), and alginic acid (b)

2.2 Preparation of pullulan/alginate blends

Blends were prepared by solution blending of pullulan and alginate in different weight ratios. The pullulan and alginate solutions were prepared by dissolving pullulan and alginate (5 wt%) in distilled water at 50 °C, under stirring (1200 rpm) for 2 h. Composite pullulan/alginate films were prepared by mixing of solutions in different weight ratios (1:1, 1.5:1, and 2:1). Glycerol was used as a plasticizer in the amount of 30 wt% per total biopolymers mass. The films were obtained by casting of solutions on Petri dishes and drying at 50 °C in a vacuum drying oven. The applied combinations of the pullulan and alginate produced a good blend uniform films and the photograph of the dried sample of edible film Pul/Alg 2:1 is shown in Figure 2.

Different weight ratios of pullulan and alginate were prepared to investigate their influence on the rheological properties of prepared blends. The pullulan/alginate blends were denoted as Pul/Alg 1:1, Pul/Alg 2:1 and Pul/Alg 1.5:1 according to different mass ratios of pullulan to alginate as shown in Table 1.

Table 1: Composition of pullulan/alginate blends

Sample	Pullulan (g)	Alginate (g)	Amount of plasticizer (wt%)
Pul/Alg 1:1	1.00	1.00	30
Pul/Alg 2:1	1.33	0.67	30
Pul/Alg 1.5:1	1.20	0.80	30

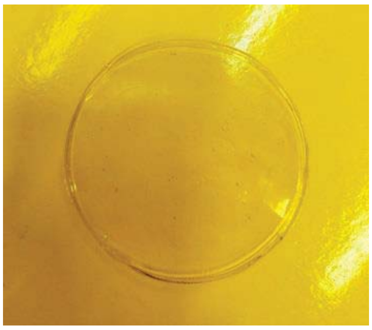


Figure 2: Photograph of the pullulan/alginate film (sample Pul/Alg 2:1)

2.3 Rheological measurements

The rheological properties of film-forming pullulan-alginate solutions were carried out by Haake Mars rheometer (Thermo Scientific, Karlsruhe, Germany) equipped with a cone-plate geometry at 25°. Steady–state measurements were performed at a shear rate from 1 to 100 s^{-1}. Two dynamic studies were performed:

a) frequency sweep test, over a range of 0.1 to 10 Hz
b) amplitude sweep test at a constant frequency of 0.1 Hz, over a range of 0.05 to 400 Pa.

Storage or elastic modulus (G', Pa) and viscous or loss modulus (G", Pa) were monitored in the function of linear frequency and stress in order to obtain mechanical spectra.

3. RESULTS AND DISCUSSION

The rheological measurements have shown that obtained solutions display thixotropic behavior (Figure 3), and the viscosity of solutions decreases with increasing in pullulan amount.

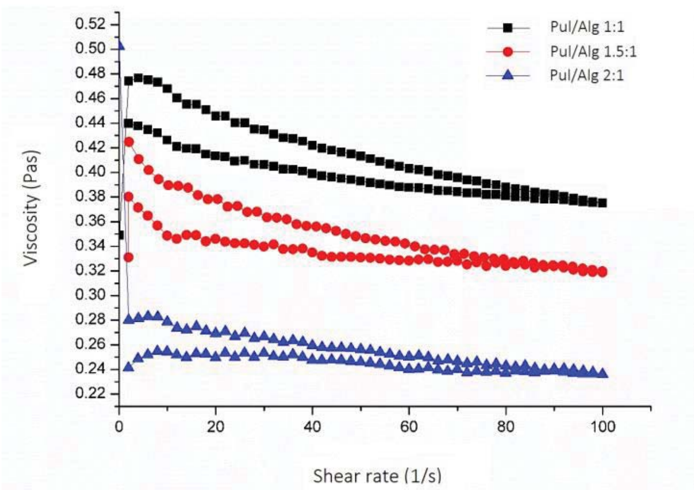
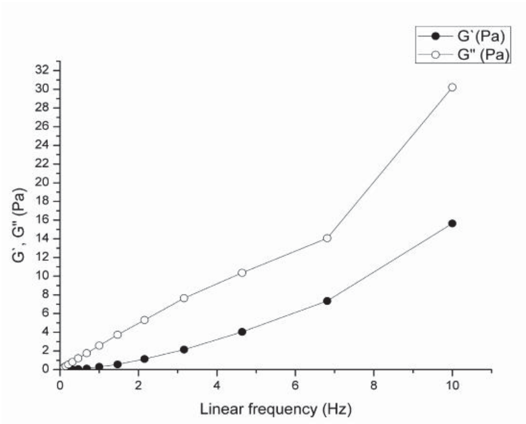


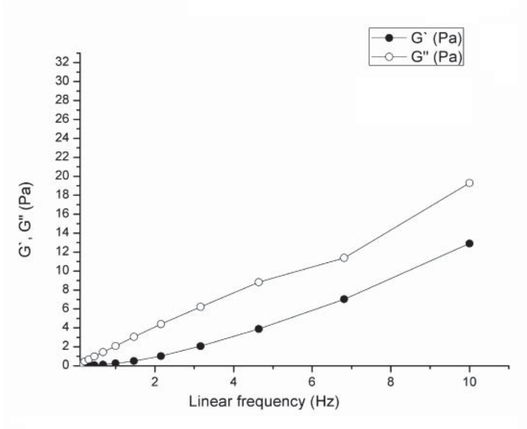
Figure 3: Steady rheological behavior of composite solutions at different Pull/Alg weight ratios

The values of elastic (G`) and viscous modulus (G”) increase with increasing in linear frequency. The greatest values of moduli are recorded for the sample with the lowest value of pullulan (1:1) (Figure 4 a). Results of the amplitude sweep test are shown in Figure 5. Elastic modulus values decrease with an increase in shear stress, while the viscous modulus is practically independent of stress over the whole investigated range (Figure 5). Considering the higher values of viscous moduli over the whole frequency and shear stress range, low and constant elastic modulus values, prepared solutions show typical viscous behaviour.



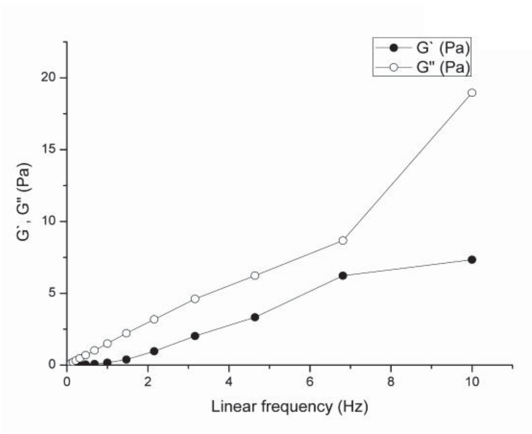
Pul/Alg 1:1

a)



Pul/Alg 1.5:1

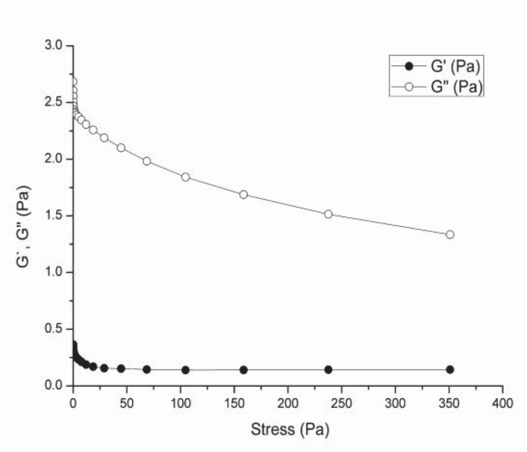
b)



Pul/Alg 2:1

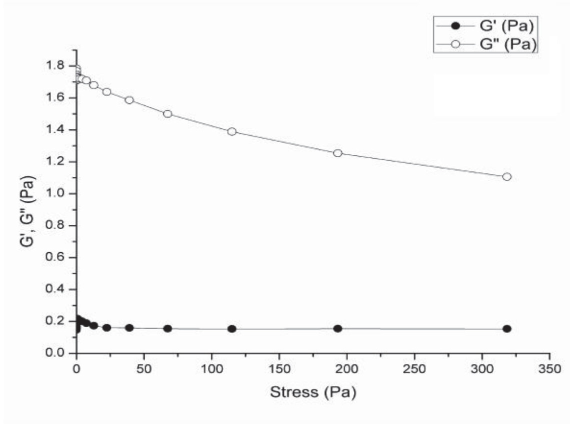
c)

Figure 4: Variation of shear elastic and viscous moduli versus frequency for pullulan/alginate film-forming solutions (a - sample Pul/Alg 1:1, b - sample Pul/Alg 1.5:1, and c - sample Pul/Alg 2:1)



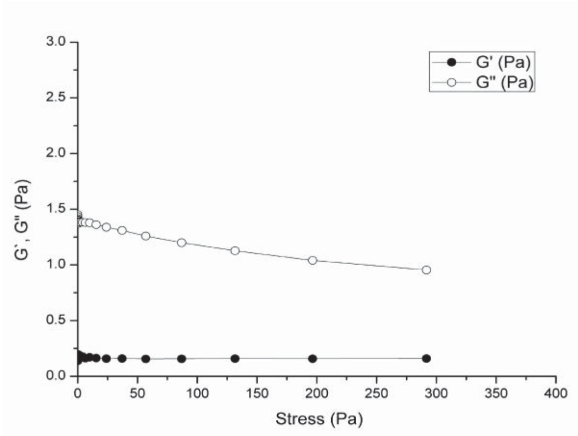
Pul/Alg 1:1

a)



Pul/Alg 1.5:1

b)



Pul/Alg 2:1

c)

Figure 5: Variation of shear elastic and viscous moduli versus shear stress for pullulan/alginate film-forming solutions (a - sample Pul/Alg 1:1, b - sample Pul/Alg 1.5:1, and c - sample Pul/Alg 2:1)

4. CONCLUSION

The main objective of this paper was to investigate the properties of different blending ratios of pullulan/alginate edible packaging films. The rheological behavior of the prepared film-forming solutions was evaluated. The steady shear and dynamic rheological measurements have shown that composite blend exposes non-Newton, shear-thinning behaviour. The results of dynamic rheological measurements have shown a dominant viscous behaviour. The greatest values of apparent viscosity and viscous moduli were observed for blend with pullulan/sodium alginate ratio 1:1.

5. ACKNOWLEDGEMENTS

The authors thank the Ministry of Education, Science and Technological Development, Republic of Serbia, projects number 451-03-68/2022-14/ 200134 and 451-03-68/2022-14/ 200222 for financial support.

6. REFERENCES

Apriliyani, M. W., Rahayu, P. P. & Thohari, I. (2022) Different Type of Application Edible Coatings Technique on Beef of Physcochemical an Sensory Quality. *Jurnal Penelitian Pendidikan IPA.* 8 (2), 534-540. Available from: doi: 10.29303/jppipa.v8i2.1142

Chen, C.-H., Kuo, W.-S. & Lai, L.-S. (2009) Rheological and physical characterization of film-forming solutions and edible films from tapioca starch/decolorized hsian-tsao leaf gum. *Food Hydrocolloids*. 23, 2132-2140. Available from: doi: 10.1016/j.foodhyd.2009.05.015

Erceg, T., Vukić, N., Šovljanski, O., Stupar, A., Šergelj, V., Aćimović, M., Baloš, S., Ugarković, J., Šuput, D., Popović, S. & Rakić S. (2022) Characterization of Films Based on Cellulose Acetate/Poly(caprolactone diol) Intended for Active Packaging Prepared by Green Chemistry Principles. *ACS Sustainable Chemistry & Engineering.* 10 (28), 9141-9154. Available from: doi: 10.1021/acssuschemeng.2c02009

Giancone, T., Torrieri, E., Pierro, P. D., Mariniello, L., Moresi, M., Porta, R. & Masi, P. (2008) Role of constituents on the network formation of hydrocolloid edible films. *Journal of Food Engineering*. 89, 195-203. Available from: doi: 10.1016/j.jfoodeng.2008.04.017

Janjarasskul, T. & Krochta J. M. (2010) Edible packaging materials. *Annual Review of Food Science and Technology.* 1, 415-448. Available from: doi: 10.1146/annurev.food.080708.100836

Jung, H. H. (2014) Edible Films and Coatings: A Review. In: Jung H. H. (ed.) *Food Science and Technology, Innovations in Food Packaging (Second Edition)*. Academic Press, pp. 213-255.

Ma, Q., Du, L., Yang, Y. & Wang, L. (2017) Rheology of film-forming solutions and physical properties of tara gum film reinforced with polyvinyl alcohol (PVA). *Food Hydrocolloids*. 63, 677-684. Available from: doi: 10.1016/j.foodhyd.2016.10.009.

Silva-Weiss, A., Bifani, V., Ihl, M., Sobral, P. J. A. & Gómez-Guillén, M. C. (2013) Structural properties of films and rheology of film-forming solutions based on chitosan and chitosan-starch blend enriched with murta leaf extract. *Food Hydrocolloids.* 31, 458-466. Available from: doi: 10.1016/j.foodhyd.2012.11.028

Tong, Q., Xiao, Q. & Lim L.-T. (2008) Preparation and properties of pullulan–alginate–carboxymethylcellulose blend films. *Food Research International*. 41, 1007-1014. Available from: doi: 10.1016/j.foodres.2008.08.005