

Experimental investigation of moisture and tensile properties of shellac and chitosan films for packaging applications

U. Vrabič Brodnjak

University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Graphic Arts and Design, Aškerčeva 12, 1000 Ljubljana, Slovenia

Received August 13, 2018; Revised September 13, 2018

Transparent films of chitosan and shellac (from *Kerria Lacca* (Kerr) Lindinger (Coccidae)) were prepared using three different amounts of plasticizers. Poly (ethylene glycol) (PEG) was used for shellac films and glycerol was a plasticizer for chitosan films. The aim of the research was to obtain improved water vapour, moisture, tensile and optic properties of films, when different amounts of plasticizers were added. The study demonstrates that the utilization of shellac films with 15% of PEG could be an alternative in the research for a sustainable packaging. The same trend was shown for chitosan films, where 15% of glycerol exhibited the best properties, compared to lower amount of plasticizer. Moreover, moisture content showed a decrease proportional to the increase in thickness and plasticizers for all treated samples. The results indicated that the addition of different amounts of glycerol and PEG affects tensile properties of the resulted films. The elongation and tensile strength were gradually increased as the plasticizer amounts in both film types increased. However, the thermal stability decreased for both films.

Key words: films, packaging, *Kerria Lacca*, tensile properties, thickness, water vapour permeability

INTRODUCTION

These days, plastics are still widely used as packaging material, due to their ability to preserve the sensory properties and nutritional values of food products [1]. On the other hand, there are high demands for the utilisation of natural polymer sources as food packaging materials [2, 3]. Natural polymers are conserved as alternatives to synthetic plastics and a lot of research has been done on the application on biopolymers in many fields [4-9]. Since food packaging materials require non-toxicity, good moisture, water, mechanical and chemical properties, many biopolymers cannot conquer to plastic materials, such as polyethylene, polypropylene, etc. Therefore good selection, production and preparation of biopolymers should be performed and implemented as food packaging. A natural polymer which is already used in many fields, including in packaging, is shellac. It is a natural polymer, obtained from purified resinous secretion, by the insects *Kerria Lacca* (Kerr) Lindinger (Coccidae). This species is the most important lac insect, being a main source of lac for the production of shellac. The insect is mostly cultivated on host trees in Thailand, India and Myanmar [9, 10]. Shellac's chemical structure is composed of hard and soft resin of polyesters and single esters containing hydroxyl and carboxyl groups [11-13]. It is widely used as an adhesive, thermoplastic, insulating material, sealant and as coating in pharmaceutical and agronomical

industries [13]. Shellac has excellent film forming and barrier properties. It is soluble in alcohol and alkaline solutions [11]. Therefore it has been widely used in the food and agro industries for gas, moisture, water and microbial protection of food products [11, 13-15].

Chitosan is known as a non-toxic biopolymer derived from the deacetylation of chitin [16]. Due to its high crystallinity, hydrogen bonds between molecular chains, which exhibit good oxygen properties, it has also attracted a lot of interest in packaging field [16-19]. Due to the positive charge on the amino group under acidic conditions, chitosan binds negatively charged molecules and therefore represents a greater barrier against grease [20-22]. Good barrier properties (antimicrobial, mechanical, against grease, oxygen), chitosan coatings can be used also as barriers in packaging [21]. Both chitosan and shellac have certain barrier properties and could be used as films in the packaging filed as replacement of plastic film barriers.

This research shows the preparation, characterisation and comparison of two different types of biopolymers, using different amounts of plasticizers. Our research is focused on film properties that are important for packaging materials. The aim of this work is to investigate moisture barrier properties and tensile properties of chitosan and dewaxed shellac flakes, using 3 different amounts of glycerol and poly (ethylene) glycol as plasticizers, which could be used as packaging materials.

* To whom all correspondence should be sent:
E-mail: urska.vrabc@ntf.uni-lj.si

EXPERIMENTAL

Methods

Materials

Shellac, refined product obtained from LAC, the resinous secretion of the female insect *Kerria Lacca* (Kerr) Lindinger (Coccidae), was supplied from A. F. Suter & Co Ltd. Company, Essex, United Kingdom. In this analysis dewaxed Shellac HS 701 SB was used, which is the purified and bleached lac (by physical absorption) according to Regulation EU 231/2012 and its specification for E904 Shellac. Chitosan, with molecular weight 20 kDa and deacetylation degree higher than 85%, was purchased from Sigma Aldrich, Austria. Poly (ethylene glycol) (PEG), with molecular weight 200, obtained from Acros Organic, Belgium and glycerol, purchased from Sigma Aldrich, Austria were added as plasticizers. Ethanol (96%) was obtained from Sigma Aldrich, Austria.

Preparation of film forming solution and casting of the films

The shellac solution was prepared by dissolving 2 g of shellac flakes in 100 ml of ethanol and different amounts of PEG 200 (2, 5 and 15% w/w) were added as a plasticiser. The solution was mixed at room temperature for 30 min until no flakes were dispersed. After that, the film solution was filtered through a polyester screen (mesh no. 140 with mesh opening of 160 μm) with aspiration to remove small lumps in the solution.

After the aspiration and the treatment, the shellac solution was casted onto petri dishes (50 ml), spread thinly, uniformly and dried at 55 °C for 10 h. After the films were peeled off from the dishes, they were cooled at room temperature (23 °C; 55% RH).

The chitosan solution was prepared by dissolving 2 g of chitosan in 100 ml (2% w/w) acetic acid and glycerol (G) (2, 5 and 15% w/w) was added as a plasticiser. The solution was mixed at 85 °C for 10 min until no chitosan was dispersed. After that it was cooled to room temperature. Before cooling down, the film solution was filtered through a polyester screen (mesh no. 140 with mesh opening of 160 μm) with aspiration to remove small lumps in the solution. After the aspiration, the solution was cast onto petri dishes (50 ml), spread thinly, uniformly and dried at 55 °C for 10 h. After the films were peeled off from the dishes, they were cooled at room temperature (23 °C; 55% RH). The films were stored in desiccators at 60% RH for further investigations.

Thickness. The thickness of films was measured with a precision digital micrometre Mitutoyo Corporation, Japan, to the nearest 0.0001 mm at 5 random locations on each film.

Water vapour permeability (WVP) and moisture. To determine the WVP of films, the ASTM E96 standard desiccant method was used. The test cups were filled with silica gel (RH = 16% in the cup), where a sample was placed between the cup and the ring cover of each cup. There was an air gap of 11 mm between the silica gel and the underside of the placed film. To ensure the best results of WVP, a silicone sealant was applied around the cup edge. The films with an exposed area of 50 cm² were tested at 50 \pm 2% RH and 40 \pm 2 °C for 24 h. Two replicas per film were tested.

Moisture of the samples was analysed according to the standard method, by measuring weight loss upon drying in a laboratory oven at 105 \pm 1 °C until constant weight. Five samples per each film were tested and the results were expressed in percentage.

Tensile properties. Tensile strength (TS) and elongation at break (E) of the films were determined on a tensile testing machine Instron 6022. The samples were analysed in standard atmosphere at a temperature of 23 °C \pm 1 °C and relative humidity of 55% \pm 2%. The cross speed head was 0.15 mm/s. Films of 6 cm in length and 0.7 cm in width were used, and a minimum of five probes for each sample was tested. During sample stretching, several load and elongation data per second were recorded until a break of the sample occurred.

Colour. The film colour was determined using the CIE colorimeter X-rite. The CIE Lab scale was used to determine L*, a* and b* colour values. A standard plate was used as the standard (L* = 92.82, a* = -1.24, b* = 0.5). Fifteen measurements for each specimen at different locations on samples were made. Before the colour measurements, the samples were conditioned at 55% RH and 25 \pm 2 °C for 72 h.

The total colour difference (ΔE) was calculated with the following equations [8]:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

$$\Delta L^* = L^* - L_0^*$$

$$\Delta a^* = a^* - a_0^*$$

$$\Delta b^* = b^* - b_0^*$$

Thermal stability. Thermal stability of shellac and chitosan films was determined using a Mettler apparatus, with heating plate Hot stage FP 82 HT. The change of phase was determined, using optical microscope. Measurement conditions were: starting

temperature 25°C, heating speed: 2°C/min and end temperature 150°C. For each sample 25 measurements were done.

RESULTS AND DISCUSSION

Shellac is one of the thermosetting resins of animal origin. The functional properties of films were investigated as function of thickness, water vapour permeability, tensile properties and plasticizer content. Chitosan has been already successfully studied as packaging material. The application of shellac and chitosan films as

packaging materials has good potential, still some more research should be done in this direction.

Thickness, moisture and water vapour permeability

The thickness of the films influences water vapour properties. For food packaging materials it is of great importance to achieve water vapour permeability (WVP) as low as possible, where high WVP determines poor moisture and water barrier properties. In our research, the thickness (mean values) of the analysed samples were used in the calculations for WVP.

Table 1. Determination of thickness, moisture content and water vapour permeability (WVP) of shellac and chitosan films with different amounts of plasticizers-glycerol (G) and poly (ethylene glycol) (PEG).

Sample	Plasticizer/ percentage (%)	Thickness (μm)	Moisture content (%)	WVP ($\text{g}/\text{m}^2\cdot\text{day}$)
Shellac	PEG 200/2	233 \pm 3.0a	4.51 \pm 0.23a	2.17 \pm 0.74b
	PEG 200/5	230 \pm 2.9a	3.18 \pm 0.28a	1.85 \pm 0.08b
	PEG 200/15	232 \pm 1.5a	2.55 \pm 0.44a	0.82 \pm 0.25b
Chitosan	G/2	230 \pm 2.5a	10.1 \pm 0.71a	7.39 \pm 0.09b
	G/5	232 \pm 2.0a	9.64 \pm 0.15a	6.52 \pm 0.63b
	G/15	230 \pm 3.1a	8.78 \pm 0.49a	5.14 \pm 0.17b

^a Means of five replicas \pm standard deviation; ^b Means of three replicas \pm standard deviation

The thickness of films influences water vapour properties [23, 24]. The water vapour permeability of films for food packaging should be as low as possible, where high WVP determines poor barrier properties. The nature of the films from biopolymers is mostly hydrophilic; therefore, the thickness influences water barrier and mechanical properties. In our research, the thickness (mean values) of films was used in the calculations for water vapour properties (TS). Table 1 shows a comparison of shellac and chitosan films with different plasticizers and their contents in the films.

From the literature it is known that glycerol is hydrophilic and improves moisture/barrier properties [5]. In our research, glycerol as a plasticiser was added in chitosan films, whereas the shellac is not miscible with glycerol and thus cannot be used as plasticizer of the lacs. Therefore PEG was used as a model plasticizer because of its compatibility with shellac.

From the obtained results it can be seen that the best water vapour properties characterise the shellac film with 15% of PEG (0.82 \pm 0.25 g mm/m²/day kPa, i.e. they are five times lower in comparison with chitosan films with the same amount of plasticizer). The same trend is detected at lower amounts of plasticizer for all samples. The results showed better moisture barrier properties of shellac films and demonstrated that the application as a packaging material in the food area can be effective

and at the same time avoiding the use of oil-derived products.

Previous research has explained that chitosan films have good oxygen but poor water vapour barriers, which is due to their hydrophilic character, which was also proved in our research [20–23].

Tensile properties

Good tensile properties such as elongation at break and tensile strength are important parameters for packaging films, due to the handling and shipping of products. Analysed films were flexible, with appropriate manageability.

Tensile strength and elongation at break were determined to estimate the effect of plasticizers on shellac and chitosan films. The results are displayed in figure 1. Compared to the tensile strength of shellac films, which varies from 24.87 to 32.88 MPa, the tensile strength of chitosan films is lower (up to 18.44). The results also show that application of different amounts of glycerol or PEG significantly improved tensile properties of all samples. However, in these cases, the results did not allow displaying the effects of PEG in chitosan films and glycerol in shellac films, which was explained earlier. Consequently, the elongation at break increased for all samples with increased amount of plasticizer. For shellac films it increased by approximately 20% and for chitosan films with 15% of glycerol, elongation increased by 13 %.

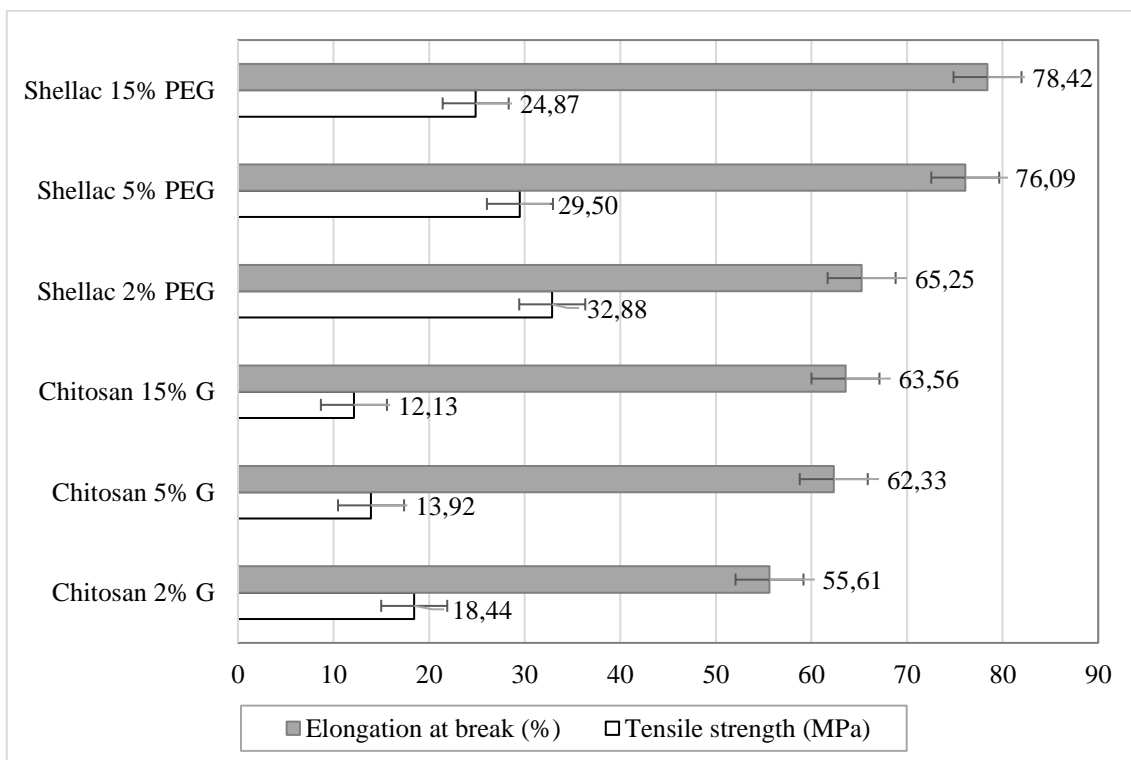


Fig. 1. Tensile strength and elongation at break for shellac and chitosan with different amounts of plasticizers.

Table 2. Colour values ($L^*a^*b^*$) and colour differences (ΔE), chroma (C) and hue angle (H) of shellac and chitosan films.

	Sample	L^*	a^*	b^*	ΔE	C	H
Shellac	PEG 200/2	84.40	1.12	37.79	/	/	/
	PEG 200/5	78.91	2.83	50.45	12.11	10.80	9.09
	PEG 200/15	77.56	3.09	48.72	11.41	9.14	14.29
Chitosan	G/2	84.06	1.19	32.36	/	/	/
	G/5	83.32	0.93	30.58	1.9	1.80	8.33
	G/15	82.52	1.40	33.02	1.7	0.65	20.01

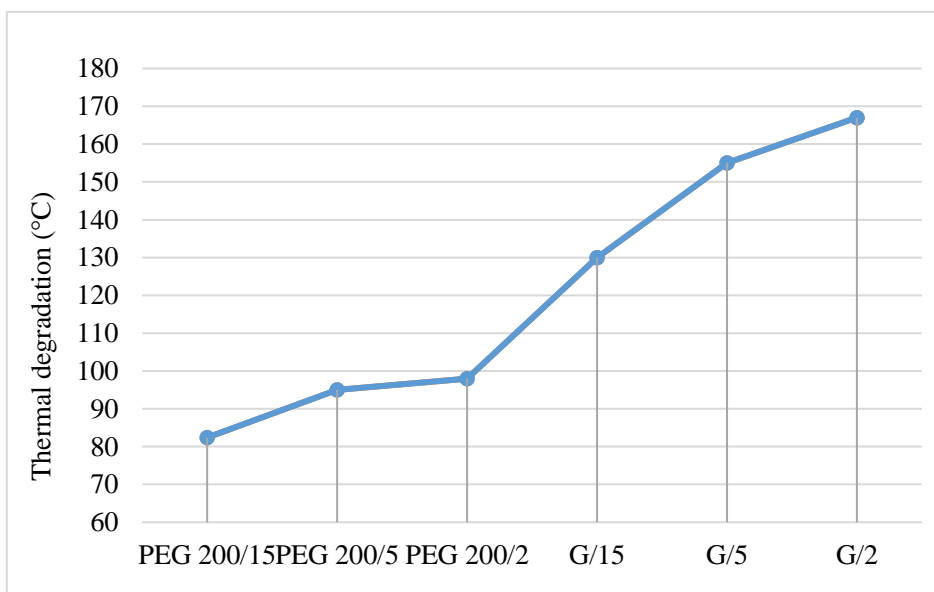


Fig. 2. Thermal stability of shellac and chitosan films with different amounts of plasticizers.

It may be assumed that in the case of the higher amount (15% w/w) of plasticizer it contributes to increased tensile properties which are of great importance for packaging materials. Results show that addition of PEG into shellac increases significantly the stretchability of films. The same results confirm the behaviour of glycerol in chitosan films.

Colour

The colour of films can be a factor in terms of consumer demands and it does not affect other analysed properties. The results are shown in Table 2.

Generally, colour is an important factor of the appearance of packaging materials [3, 8]. The total colour difference, chroma and hue angle were calculated from the colour values, and compared to the samples with the smallest amount of plasticizer. The aim was to compare the appearance of the films with added plasticizer and its effect. As expected, shellac is more yellow compared to chitosan, since the prime component, shellac flakes, are yellow. With added plasticizer to both samples, lightness increased, as seen from table 2. Colour differences between shellac films are bigger, due to uneven flakes colour. Chitosan was applied as powder with more even colour appearance. The a^* and b^* values significantly vary between all samples. From the colour analysis it was confirmed that shellac films were much more yellow than chitosan films.

Thermal stability

Thermal stability of analysed samples is shown in Figure 2. It can be seen that each film has similar thermal properties. For shellac films with the highest amount of PEG a change in appearance of the films was shown at 82°C. For a sample with 2% of PEG added, the thermal stability was higher. For chitosan films the results were similar. This indicated that the presence of glycerol in the chitosan structure caused the chitosan polymer to break more easily. From the literature it was proven that glycerol reduces intermolecular hydrogen bonding of chitosan backbone, thus weakening the bond between the polymer chains [25]. Compared to shellac films, chitosan is more stable and achieved higher thermal stability, up to 167°C.

CONCLUSIONS

A study on the potential of using shellac and chitosan as packaging films was carried out. The most significant results obtained were: reduction of water vapour permeability and improvement in

tensile strength, when the amount of plasticizer increased for both film types. Moreover, the tensile properties of all tested films were good and sufficient for the use in the packaging field. Although the colour of shellac films is quite yellowish, it could be more appropriate from the consumer side as a barrier film. As expected, thermal stability decreased with increased amount of plasticizers in both types of films.

The study demonstrates that the utilization of shellac films with 15% of PEG could be an alternative in the search for a sustainable packaging. Still some more research should be done, regarding barrier properties such as grease, oxygen permeability, migration etc. Compared to chitosan films, shellac is already a food additive and therefore is not harmful for human health and from our research, exhibited better properties.

Acknowledgement: This research was supported by the COST action CA15216 (ENBA). The author would like to thank Mr. Manfred Penning and Mr. Stephen Hall from the A. F. Suter & Co Ltd. Company, Essex, United Kingdom, for the Shellac supplement. We would also like to thank University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles Graphic Arts and Design, Ljubljana, Slovenia for financial support.

REFERENCES

1. G. G. Buonocore, M. A. Del Nobile, A. Panizza, M. R. Corbo, L. Nicolais, *J. Controlled Release*, **90**, 97 (2003).
2. P. Appendini, J. H. Hotchkiss, *Innovative Food Science & Emerging Technologies*, **3**, 113, (2002).
3. U. Vrabič Brodnjak, *Prog. Org. Coat.*, **103**, 93 (2017).
4. W. Zhang, H. Xiao, L. Qian, *Carbohydr. Polym.*, **101**, 401 (2014).
5. P. C. Srinivasa, M. N. Ramesh, K. R. Kumar, R. N. Tharanathan, *J. Food Eng.*, **63**, 79 (2004).
6. C. Wu, S. Peng, C. Wen, X. Wang, L. Fan, R. Deng, J. Pang, *Carbohydr. Polym.*, **89**, 497 (2012).
7. D. A. Todorova, S. P. Bencheva, *Bulg. Chem. Comm.*, **47**, 45 (2015).
8. U. Vrabič Brodnjak, *Prog. Org. Coat.*, **112**, 86 (2017).
9. S. Soradech, J. Nunthanid, S. Limmatvapirat, M. Luangtana-anan, *Food Control*, **73**, 1310 (2017).
10. Y. Farag, C. S. Leopold, *Dissolut. Technol.*, **16**, 33 (2009).
11. S. Soradech, J. Nunthanid, S. Limmatvapirat, M. Luangtana-anan, *Food Control.*, **108**, 94 (2012).
12. F. Debeaufort, D. Luu, A. Voilley, *J. Membrane Sci.*, **325**, 277 (2008).
13. S. C. Shit, P. M. Shah, *J. Polym.*, **2014**, 13 (2014).
14. M. Penning, *Seifen Öle Fette Wachse*, **6**, 221 (1990).

15. Luangtana-anan, J. Nunthanid, S. Limmatvapirat, *J. Agr. Food. Chem.*, **58**, 12934 (2010).
16. N. Bordenave, S. Grelier, V. Coma, *Biomacromolecules* **11**, 88, (2010).
17. X. Y. Xu, K. M. Kim, M. A. Hanna, D. Nag, *Ind. Crop. Prod.*, **21**, 185, (2005).
18. U. Vrabič Brodnjak, A. Jesih, D. Gregor-Svetec, *Coatings*, **8**, 133 (2018).
19. M. S. Rao, S. R. Kanatt, S. P. Chawla, A. Sharma, *Carbohydr. Polym.*, **82**, 1243, (2010).
20. F. Ham-Pichavant, G. Sèbe, P. Pardon, V. Coma, *Carbohydr. Polym.*, **61**, 259, (2005).
21. S. Wang, Y. Jing, *BioResources*, **11**, 1868, (2016).
22. M. Jaworska, K. Sakurai, P. Gaudon, E. Guibal, *Polym. Int.*, **2**, 198 (2003).
23. S. Rivero, M. A. García, A. Pinotti, Composite and bi-layer films based on gelatin and chitosan, *Journal of Food Engineering*, **90**, 531 (2009).
24. K. Cooksey, K. Marsh, L. Doar, Predicting permeability & transition rate for multilayer materials, *Food Technology*, **53**, 60 (1999).
25. E. Susilowati, I. Kartini, S. J. Santosa, S. J., in: IOP Conference Series: Materials Science and Engineering, IOP Publishing, 2016, vol. 107, No. 1, p. 12041.