

Preparation and characterization of starch/carrageenan edible films

Abdou, E. S. and *Sorour, M. A.

*Food Engineering and Packaging Department, Food Technology Research Institute,
Agriculture Research Center, Giza, Egypt*

Article history

Received: 25 June 2013

Received in revised form:

1 September 2013

Accepted: 5 September 2013

Keywords

Rheological properties

Starch

Carrageenan

Mechanical properties

Water vapor permeability

Abstract

The mechanical and water vapor permeability of starch/carrageenan cast films were investigated, the rheological properties of starch/carrageenan blends were also studied. The blends were prepared by different concentrations of starch and carrageenan. Three concentration of starch (0.75%, 1% and 1.25%) and two concentrations of carrageenan (0.5% and 0.75%) were used with adding 0.5% glycerol as plasticizer the results show that all samples behaves as non-Newtonian pseudoplastic fluid and obeys the power law relationship. The mechanical and water vapor permeability of the cast films increase with increasing carrageenan content.

© All Rights Reserved

Introduction

Recently, considerable research has been conducted to develop and apply bio based polymers made from a variety of agricultural commodities and/or of food waste products (Vasconez *et al.*, 2009). This increased interest was intensified due to concerns about limited natural resources of the fossil fuel reserve and the environmental impact caused by the use of non-biodegradable plastic-based packaging materials (Catarina *et al.*, 2009). Such biopolymers include starches, cellulose derivatives, chitosan/chitin, gums, proteins (animal or plant-based) and lipids (Cutter, 2006 and Elsabee and Abdou, 2013). These materials offer the possibility of obtaining thin films and coatings to cover fresh or processed foods to extend their shelf life. Edible films and coatings offer extra advantages such as edibility, biocompatibility, esthetic appearance, barrier to gasses properties, non-toxicity, non-polluting and its low cost (Han, 2000). In addition, bio-films and coatings, by themselves are acting as carriers of foods additives (i.e.: antioxidants, antimicrobials), and have been particularly considered in food preservation due to their ability to extend the shelf life (Sallam, 2007).

Starch is a natural polymer that can readily be cast into films. It consists of (1-4) linked α -D-glucopyranosyl units, two kinds of chain are present in natural starch: amylopectin and amylose. The linear polymer, amylose, makes up about 20 wt% of the granule, and the branched polymer, amylopectin, the remainder. Amylose is crystalline and can have an average molecular weight as high as 500,000, while amylopectin is highly branched and have very

high molecular-weight (Chandra and Rustgi, 1998). Despite their ease of preparation, starch films have poor physical properties. These can be improved by blending with either synthetic polymers to produce biodegradable materials (Lawton and Fanta, 1994) or other natural polymers in edible packaging (Arvanitoyannis *et al.*, 1996; Psomiadou *et al.*, 1996; Arvanitoyannis *et al.*, 1998a; Arvanitoyannis, 1998b).

Red seaweeds produce different types of sulfated polysaccharides, as carrageenans (Noseda and Cerezo, 1995; Chiovitti *et al.*, 2004; Viana *et al.*, 2004; Falshaw *et al.*, 2005). The carrageenans are a family of sulfated, linear polysaccharides that occur in the cell wall and intercellular matrix of numerous species of red seaweeds (Rhodophyta) (Therkelsen, 1993; Knutsen *et al.*, 1994). Their primary structures are based on an alternating disaccharide repeating sequence of β -D-galactose linked at position 3, and α -D-galactoselinked at position 4. Carrageenans have extensive industrial applications as thickeners, stabilizers and gelling agents in food and related products (such as cosmetics, toiletries and toothpaste).

Several isomers of carrageenan are known as κ -, λ -, and ι -carrageenan (κ -kappa, λ - lambda and ι -iota), and they differ in the number and position of the ester sulfate groups on the repeating galactose units (Zablackis and Santos, 1986). κ -carrageenan has only one negative charge per disaccharide with a tendency of forming a strong and rigid gel. κ -carrageenan has two and λ -carrageenan bears on the average 2.7 charges per disaccharide unit. The gelling power of κ -carrageenan enhances its good film forming ability

*Corresponding author.

Email: manal.sorour@yahoo.com

(Park *et al.*, 2001; Briones *et al.*, 2004; Choi *et al.*, 2005).

Blending of starch with κ -carrageenan results in the formation of edible coating with good film forming and mechanical properties, starch must be gelatinized first before blending with carrageenan. Rheology concerns with the flow and deformation of substances and, in particular, to their behavior in the transient area between solids and fluids. Moreover, rheology attempts to define a relationship between the stress acting on a given material and the resulting deformation and/or flow that takes place (Gipsy and Gustavo, 2005)

Knowledge of the rheological properties of food products is important for design and process evaluation, process control, and consumer acceptability of a product. In addition, the characterization of time-dependent rheological properties of food systems is important to establish relationships between structure and flow, and to correlate physical parameters with sensory evaluation (Figoni and Shoemaker, 1983). When a material is sheared at a constant shear rate, the viscosity of a thixotropic material will decrease over a period of time, implying a progressive breakdown of structure. Rheopectic materials manifest the opposite sort of behavior. The food products containing polymers exhibit thixotropic behavior, such as for concentrated yogurt, milled sesame, milled black cumin paste and mayonnaise (Basim, 2003).

Time dependent flow behavior can be investigated as a function of time throughout tests where both the degree of shear load and the measuring temperature are preset as constant values. Foods such as suspensions, emulsions and foams are time dependent fluids and show thixotropy and rheopecty behavior. Thixotropic behavior means the reduction in structural strength during the shear load phase and the more or less rapid, but complete structural regeneration during the subsequent rest phase (Mezger, 2002). As starch and carrageenan blends can be used as edible film and coating we have investigated the preparation and characterization of starch/carrageenan blends and the obtained edible films.

Material and Methods

Raw materials

Starch was obtained from (NENTEHCH LTD, BRIXWORTH, NORTHANTS.U.K.). Carrageenan was obtained from Mefad company (Giza, Egypt).

Gelatinization of starch solution in microwave

Starch was gelatinized first in microwave before

blending with carrageenan. Starch samples with predetermined starch concentrations, was prepared by using starch and distilled water, the samples were stirred gently just before heating them in the microwave oven in order to ensure that the starch was fully suspended in the water. Starch samples (150 ml) were heated at full power in the microwave oven WP800 for approximately 3 minutes.

Blend formation

Starch was blended with Carrageenan by different ratios of starch and carrageenan using glycerol as plasticizer. Starch was gelatinized in 150 ml distilled water and carrageenan dissolved in 50 ml distilled water so the total volume of the blend was 200 ml. The different formulas of the blends were as follows: Sample 1 (0.75% starch + 0.75% carrageenan), sample 2 (0.75% starch + 0.5% carrageenan), sample 3 (1% starch + 0.75% carrageenan), sample 4 (1% starch + 0.5% carrageenan), sample 5 (1.25% starch + 0.75% carrageenan) and sample 6 (1.25% starch + 0.5% carrageenan).

Rheological properties

The rheological properties of the prepared blends were studied to investigate the flow behavior of blends which is an important factor for food coating materials. Rheological parameters (shear stress, shear rate, viscosity) of starch/carrageenan blends were measured at different temperatures using Brookfield Engineering labs DV-III Rheometer. The blend was placed in a small sample adapter and a constant temperature water bath was used to maintain the desired temperature. The viscometer was operated between 10 and 50 rpm and shear stress, shear rate, viscosity data were obtained directly from the instrument, the SC4-21 spindle was selected for the measurement. Rheological measurements were made at different concentrations of starch and carrageenan and different time of shearing.

Film formation of starch/carrageenan

Different concentrations of starch and carrageenan were blended using glycerol as plasticizer, The mixtures were cast onto flat, leveled, non-stick Teflon plates (20 cm x 15 cm) then the plates were held at 50°C for 10 hr. undisturbed and then cooled to the ambient temperature before peeling the films off from the plates.

Water vapor permeability of starch/carrageenan films

Water vapor permeability of the films was

measured using ASTM-E 96/1980 (38°C/90%).

Mechanical properties

Tensile strength and elongation of starch/carrageenan films were measured using an Instron Testing Machine model 1195 England using Load Range 2500 N, Sample Length 25 mm. The reported values are the average of four measurements.

Results and Discussion

Rheological properties of starch/carrageenan blends

The flow curves (shear rate versus shear stress) of Starch/carrageenan blends with 0.5% glycerol were plotted. Figure 1 shows that all samples behave as non-Newtonian pseudoplastic fluid. Constitutive equations are also important for providing the material parameters required by process control, the shear stress-shear rate and properties of Carrageenan/gelatinized starch blends obey the following power law relationship:

$$\tau = k \gamma^n \quad (1)$$

Where, τ is the shear stress, Pa, k is the consistency index, γ is the shear rate, 1/sec, and n is the flow behavior index.

Thixotropic effect of starch/carrageenan blends

Time dependency of the starch/carrageenan blends was evaluated by determining the change in apparent viscosity under different shear rates. All samples were found to have thixotropic behavior since viscosity increased as concentration of carrageenan increased as shown in Figure 2.

Figure 3 shows the relation between time of shearing and viscosity for Starch/carrageenan blends. Because the material is shear thinning and time dependent, the viscosity for decreases continuously with time, which means that on shearing of the material causes the aggregated particles to be disrupted and so they offer less resistance to flow and the viscosity decreases with time until a constant value. Shear stress decay data were obtained at different time and at different concentrations of starch and carrageenan the variation of shear stress with time of shearing was fitted to Weltmann model (Weltmann, 1943).

$$\tau = A - B \ln t \quad (2)$$

Where, τ is the shear stress, Pa and t is the time, s, A, B are constants.

Figure 4 shows that the shear stress was well fitted with time according to Weltmann model at

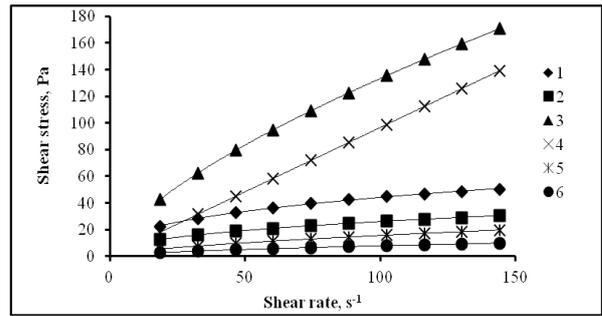


Figure 1. Effect of shear rate on shear stress for Starch/carrageenan blends

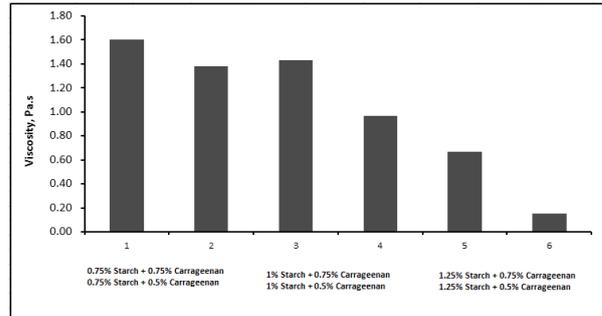


Figure 2. Effect of carrageenan concentration on apparent viscosity of the blends

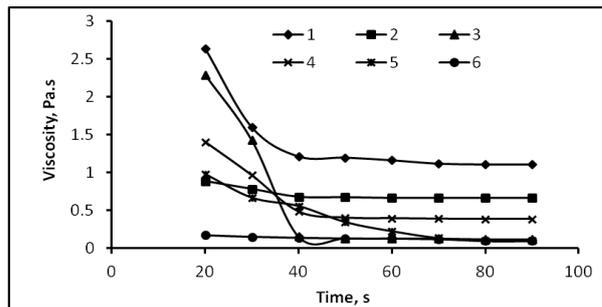


Figure 3. The relation between time of shearing and viscosity for Starch/carrageenan blends

different shear rates for sample 1. The same trend was observed for all samples studied.

Mechanical properties

Mechanical properties (tensile strength and elongation) of the starch/carrageenan based films are presented in Figures 5 and 6. The behavior of tensile strength and elongation at break varying according to the carrageenan content. The tensile strength results (Figure 5) show that tensile strength significantly increases with the increase of carrageenan content in the blend, for all films prepared. Elongation is a measure of the film's capacity for stretching. Elongation results (Figure 6) show that elongation at break increase with increasing carrageenan content in the blend for all films prepared. These results of elongation can be explained because carrageenan is more hygroscopic than starch; hence water uptake could explain the plasticization behavior (increased elongation at break) which accompanies the increase

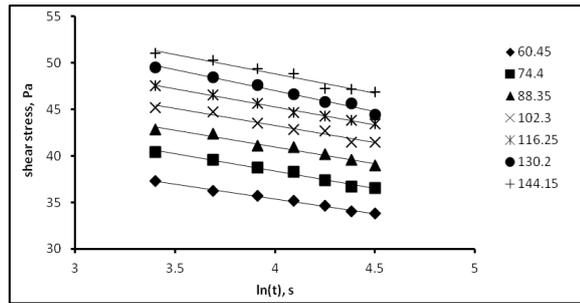


Figure 4. Relationship between shear stress and $\ln(t)$ at different shear rate for sample 1

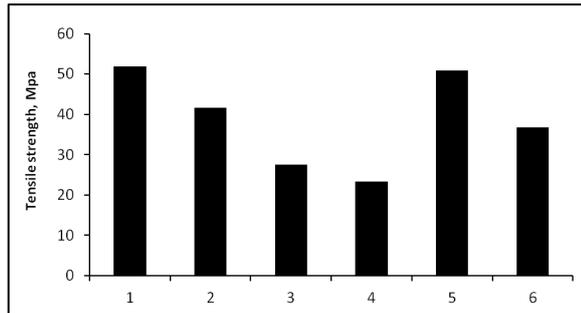


Figure 5. Tensile strength of starch/carrageenan films

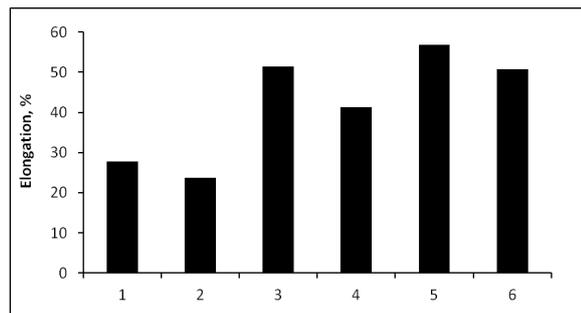


Figure 6. Elongation % of starch/carrageenan films

in carrageenan content. Similar results were observed by other authors (Larotonda, 2007).

Water vapor permeability

Starch films due to the hydrophilicity properties of the starch polymers; provide a minimal barrier to moisture. Films of polysaccharides have overall suitable mechanical and optical properties but are highly sensitive to moisture and exhibit poor water vapor barriers (Guilbert *et al.*, 1996). Water vapor permeability in carrageenan based films has a high value among other polysaccharide based films as reported in literature. Water vapor permeability values of starch/carrageenan films water vapor permeability significantly increases with increasing carrageenan percent. The results show that water vapor permeability increase from 4.4 to 4.6, 3.6 to 3.7 and 3.6 to 3.8 for samples 1, 2, 3, 4, 5 and 6 respectively.

Conclusion

From the rheological behavior of the film forming starch/carrageenan blends all samples behaves as non-Newtonian pseudoplastic behavior. Time dependency of the starch/carrageenan blends was evaluated all samples were found to have thixotropic behavior since viscosity of starch/carrageenan blends increased as concentration of carrageenan increase. The relation between time of shearing and viscosity for Starch/carrageenan blends shows that the viscosity for all samples decreases continuously with time until a constant value. Mechanical properties (tensile strength and elongation) of the starch/carrageenan based films are evaluated. The behavior of tensile strength and elongation at break varying according to the carrageenan content tensile strength significantly increases with the increase of carrageenan content in the blend, for all films prepared. Also elongation at break increase with increasing carrageenan content in the blend for all films prepared. The water vapor permeability values of starch/carrageenan films show that water vapor permeability significantly increases with increasing carrageenan percent.

References

- Arvanitoyannis, I., Biliaderis, C. G., Ogawa, H. and Kawasaki, N. 1998a. Biodegradable films made from low-density polyethylene (LDPE), rice starch and potato starch for food packaging applications: Part 1. *Carbohydrate Polymers* 36:89-104.
- Arvanitoyannis, I., Nakayama A. and Aiba, S. 1998b. Edible films made from hydroxypropyl starch and gelatin and plasticized by polyols and water. *Carbohydrate Polymers* 36:105-119.
- Arvanitoyannis, I., Psomiadou, E. and Nakayama, A. 1996. Edible films made from sodium caseinate, starches, sugars or glycerol Part 1, *Carbohydrate Polymers* 31:179-192.
- Basim Abu-Jdayil. 1983. Modelling the time-dependent rheological behavior of semisolid food stuffs, *Journal of Food Engineering* 57:97-102
- Briones, A. V., Ambal, W. O., Estrella, R. R., Pangilinan, R., De Vera, C. J. and Pacis, R. L. 2004. Tensile and tear strength of carrageenan film from Philippine *Eucheuma* species. *Marine Biotechnology* 6:148-151.
- Catarina, O., Ferreira, C.A., Delgadillo, N.I., Lopes-da-Silva, J.A. 2009. *Food Research institute* 42:807-813.
- Chandra, R. and Rustgi, R. 1998. Biodegradable Polymers. *Progress Polymer Science* 23:1273-1335.
- Chiovitti, A., Bacic, A., Craik, D. J., Kraft, G. T. and Liao, M. 2004. A nearly idealized 6'-O-methylated iota-

- carrageenan from the Australian red alga *Claviconium ovatum* (Acrotylaceae, Gigartinales) (Acrotylaceae, Gigartinales). *Carbohydrate Research* 339:1459–1466.
- Choi, J. H., Choi, W. Y., Cha, D. S., Chinnan, M. J., Park, H. J. and Lee, D. S. 2005. Diffusivity of potassium sorbate in kappa-carrageenan based antimicrobial film. *Food Science and Technology-Lebensmittel-Wissenschaft und Technologie*, 38:417–423.
- Cutter, C.N. 2006. Opportunities for bio-based packaging technologies to improve the quality and safety of fresh and further processed muscle foods, *Meat Science* 74:131–142.
- Elsabee, M. Z. and Abdou, E. S. 2013. Chitosan Based Edible Films and Coatings: A Review *Materials Science and Engineering*. 33:1819–1841
- Falshaw, R., Furneaux, R. H. and Stevenson, D. E. 2005. Structural analysis of carrageenans from the red seaweed *Callophyllis hombroniana* Mont. Kütz (Kallymeniaceae, Rhodophyta). *Carbohydrate Research* 340:1149–1158.
- Figoni, P. I. and Shoemaker, C. F. 1983. Characterization of time dependent flow properties of mayonnaise under steady shear, *Journal of Texture Studies* 14: 431–442.
- Guilbert, S., Gontard, N. and Gorris, L. G. M. 1996. Prolongation of the shelf life of perishable food products using biodegradable films and coatings, *Lebens mittel-Wissenschaft und-Technologie* 29:10–17.
- Gustavo, V. and Barbosa, C. 2005. Rheology for the food industry Gipsy Tabilo-Munizaga. *Journal of Food Engineering* 67:147–156.
- Han, J.H. 2000. Antimicrobial food packaging. *Food Technology* 54:56–65.
- Knutsen, S. H. Mylabodski, D. E., Larsen, B. and Usov, A. I. 1994. A modified system of nomenclature for red algal galactans. *Botanica Marina* 37:163–169.
- Larotonda, F. D. S. 2007. Biodegradable films and coatings obtained from carrageenan from *Mastocarpus stellatus* and starch from *Quercussuber*. Faculty of Engineering of the University of Porto. Ph.D thesis.
- Lawton, J. W. and Fanta, G. F. 1994. Glycerol-plasticized films prepared from starch-poly (vinyl alcohol) mixtures: effect of (polyethylene-co-acrylic acid). *Carbohydrate Polymers* 23:275-280.
- Maria, J. F., Pau, T. and Amparo, C. 2008. Effect of alginate and κ -carrageenan on tensile properties and water vapor permeability of sodium caseinate–lipid based films. *Carbohydrate Polymers* 74:419–426.
- Mezger, T. G. 2002. In Ulrich Zorll (Ed.). *The rheology handbook: for users of rotational and oscillatory rheometers*. Germany: Hannover.
- Noseda, M. D. and Cerezo, A. S. 1995. Alkali-modification of carrageenans. II. The cyclization of model compounds containing non-sulfated b-D-galactoseunits. *Carbohydrate Polymers* 26:1–3.
- Park, S. Y., Lee, B. I., Jung, S. T. and Park, H. J. 2001. Biopolymer composite films based on kappa-carrageenan and chitosan. *Materials Research Bulletin* 36:511–519.
- Psomiadou, E. Arvanitoyannis, I. and Yamamoto, N. 1996. Edible films made from natural resources; microcrystalline cellulose (MCC), methylcellulose (MC) and corn starch and polyols-Part 2. *Carbohydrate Polymers* 31:193-204.
- Sallam, K.I. 2007. Antimicrobial and antioxidant effects of sodium acetate, sodium lactate, and sodium citrate in refrigerated sliced salmon. *Food Control* 18:566–575.
- Sun, Y. P., Burtrand, I. L., Soon, T. J. and Hyun, J. P. 2001. Biopolymer composite films based on k-carrageenan and chitosan. *Materials Research Bulletin* 36: 511-519.
- Therkelsen, G. H. 1993. Carrageenan. In R. L. Whistler and J. N. BeMiller (Eds.), *Industrial gums* (3rd ed., pp. 145–180). San Diego, CA: Academic Press.
- Vásconez, M.B., Flores, S.K., Campos, C.A., Alvarado, J. and Gerschenson, L.N. 2009. Antimicrobial activity and physical properties of chitosan-tapioca starch based edible films and coatings. *Food Research International* 42:762–769.
- Viana, A. G., Noseda, M. D., Duarte, M. E. R. and Cerezo, A. S. 2004. Alkali modification of carrageenans. Part V. The iota- ν hybrid carrageenan from *Eucheuma denticulatum* and its cyclization to iota-carrageenan. *Carbohydrate Polymers* 58:455–460.
- Weltmann, R.N. 1943. Breakdown of thixotropic structure as function of time. *Journal of Applied Physics* 14:343-350.