

Special Issue: Bio-based Packaging

Guest Editors: José M. Lagarón, Amparo López-Rubio, and María José Fabra
Institute of Agrochemistry and Food Technology of the Spanish Council for Scientific Research

EDITORIAL

Bio-based Packaging

J. M. Lagarón, A. López-Rubio and M. J. Fabra, *J. Appl. Polym. Sci.* 2015,
DOI: 10.1002/app.42971

REVIEWS

Active edible films: Current state and future trends

C. Mellinas, A. Valdés, M. Ramos, N. Burgos, M. D. C. Garrigós and A. Jiménez,
J. Appl. Polym. Sci. 2015, DOI: 10.1002/app.42631

Vegetal fiber-based biocomposites: Which stakes for food packaging applications?

M.-A. Berthet, H. Angellier-Coussy, V. Guillard and N. Gontard, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.42528

Enzymatic-assisted extraction and modification of lignocellulosic plant polysaccharides for packaging applications

A. Martínez-Abad, A. C. Ruthes and F. Vilaplana, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.42523

RESEARCH ARTICLES

Combining polyhydroxyalkanoates with nanokeratin to develop novel biopackaging structures

M. J. Fabra, P. Pardo, M. Martínez-Sanz, A. Lopez-Rubio and J. M. Lagarón, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.42695

Production of bacterial nanobiocomposites of polyhydroxyalkanoates derived from waste and bacterial nanocellulose by the electrospinning enabling melt compounding method

M. Martínez-Sanz, A. Lopez-Rubio, M. Villano, C. S. S. Oliveira, M. Majone, M. Reis and J. M. Lagarón, *J. Appl. Polym. Sci.* 2015,
DOI: 10.1002/app.42486

Bio-based multilayer barrier films by extrusion, dispersion coating and atomic layer deposition

J. Vartiainen, Y. Shen, T. Kaljunen, T. Malm, M. Vähä-Nissi, M. Putkonen and A. Harlin, *J. Appl. Polym. Sci.* 2015,
DOI: 10.1002/app.42260

Film blowing of PHBV blends and PHBV-based multilayers for the production of biodegradable packages

M. Cunha, B. Fernandes, J. A. Covas, A. A. Vicente and L. Hilliou, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.42165

On the use of tris(nonylphenyl) phosphite as a chain extender in melt-blended poly(hydroxybutyrate-co-hydroxyvalerate)/clay nanocomposites: Morphology, thermal stability, and mechanical properties

J. González-Ausejo, E. Sánchez-Safont, J. Gámez-Pérez and L. Cabedo, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.42390

Characterization of polyhydroxyalkanoate blends incorporating unpurified biosustainably produced poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

A. Martínez-Abad, L. Cabedo, C. S. S. Oliveira, L. Hilliou, M. Reis and J. M. Lagarón, *J. Appl. Polym. Sci.* 2015,
DOI: 10.1002/app.42633

Modification of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) properties by reactive blending with a monoterpene derivative

L. Pilon and C. Kelly, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.42588

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) films for food packaging: Physical-chemical and structural stability under food contact conditions

V. Chea, H. Angellier-Coussy, S. Peyron, D. Kemmer and N. Gontard, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41850



Special Issue: Bio-based Packaging

Guest Editors: José M. Lagarón, Amparo López-Rubio, and María José Fabra
Institute of Agrochemistry and Food Technology of the Spanish Council for Scientific Research

Impact of fermentation residues on the thermal, structural, and rheological properties of polyhydroxy(butyrate-co-valerate) produced from cheese whey and olive oil mill wastewater
L. Hilliou, D. Machado, C. S. S. Oliveira, A. R. Gouveia, M. A. M. Reis, S. Campanari, M. Villano and M. Majone, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42818](https://doi.org/10.1002/app.42818)

Synergistic effect of lactic acid oligomers and laminar graphene sheets on the barrier properties of polylactide nanocomposites obtained by the in situ polymerization pre-incorporation method

J. Ambrosio-Martín, A. López-Rubio, M. J. Fabra, M. A. López-Manchado, A. Sorrentino, G. Gorrasi and J. M. Lagarón, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42661](https://doi.org/10.1002/app.42661)

Antibacterial poly(lactic acid) (PLA) films grafted with electrospun PLA/allyl isothiocyanate fibers for food packaging

H. H. Kara, F. Xiao, M. Sarker, T. Z. Jin, A. M. M. Sousa, C.-K. Liu, P. M. Tomasula and L. Liu, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42475](https://doi.org/10.1002/app.42475)

Poly(L-lactide)/ZnO nanocomposites as efficient UV-shielding coatings for packaging applications

E. Lizundia, L. Ruiz-Rubio, J. L. Vilas and L. M. León, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42426](https://doi.org/10.1002/app.42426)

Effect of electron beam irradiation on the properties of polylactic acid/montmorillonite nanocomposites for food packaging applications

M. Salvatore, A. Marra, D. Duraccio, S. Shayanfar, S. D. Pillai, S. Cimmino and C. Silvestre, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42219](https://doi.org/10.1002/app.42219)

Preparation and characterization of linear and star-shaped poly L-lactide blends

M. B. Khajeheian and A. Rosling, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42231](https://doi.org/10.1002/app.42231)

Mechanical properties of biodegradable polylactide/poly(ether-block-amide)/thermoplastic starch blends: Effect of the crosslinking of starch

L. Zhou, G. Zhao and W. Jiang, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42297](https://doi.org/10.1002/app.42297)

Interaction and quantification of thymol in active PLA-based materials containing natural fibers

I. S. M. A. Tawakkal, M. J. Cran and S. W. Bigger, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42160](https://doi.org/10.1002/app.42160)

Graphene-modified poly(lactic acid) for packaging: Material formulation, processing, and performance

M. Barletta, M. Puopolo, V. Tagliaferri and S. Vesco, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42252](https://doi.org/10.1002/app.42252)

Edible films based on chia flour: Development and characterization

M. Dick, C. H. Pagno, T. M. H. Costa, A. Gomaa, M. Subirade, A. De O. Rios and S. H. Flóres, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42455](https://doi.org/10.1002/app.42455)

Influence of citric acid on the properties and stability of starch-polycaprolactone based films

R. Ortega-Toro, S. Collazo-Bigliardi, P. Talens and A. Chiralt, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42220](https://doi.org/10.1002/app.42220)

Bionanocomposites based on polysaccharides and fibrous clays for packaging applications

A. C. S. Alcântara, M. Darder, P. Aranda, A. Ayral and E. Ruiz-Hitzky, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42362](https://doi.org/10.1002/app.42362)

Hybrid carrageenan-based formulations for edible film preparation: Benchmarking with kappa carrageenan

F. D. S. Larotonda, M. D. Torres, M. P. Gonçalves, A. M. Sereno and L. Hilliou, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42263](https://doi.org/10.1002/app.42263)



Special Issue: Bio-based Packaging

Guest Editors: José M. Lagarón, Amparo López-Rubio, and María José Fabra
Institute of Agrochemistry and Food Technology of the Spanish Council for Scientific Research

Structural and mechanical properties of clay nanocomposite foams based on cellulose for the food packaging industry

S. Ahmadzadeh, J. Keramat, A. Nasirpour, N. Hamdami, T. Behzad, L. Aranda, M. Vilasi and S. Desobry, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42079](https://doi.org/10.1002/app.42079)

Mechanically strong nanocomposite films based on highly filled carboxymethyl cellulose with graphene oxide

M. El Achaby, N. El Miri, A. Snik, M. Zahouily, K. Abdelouahdi, A. Fihri, A. Barakat and A. Solhy, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42356](https://doi.org/10.1002/app.42356)

Production and characterization of microfibrillated cellulose-reinforced thermoplastic starch composites

L. Lendvai, J. Karger-Kocsis, Á. Kmetty and S. X. Drakopoulos, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42397](https://doi.org/10.1002/app.42397)

Development of bioplastics based on agricultural side-stream products: Film extrusion of *Crambe abyssinica*/wheat gluten blends for packaging purposes

H. Rasel, T. Johansson, M. Gällstedt, W. Newson, E. Johansson and M. Hedenqvist, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42442](https://doi.org/10.1002/app.42442)

Influence of plasticizers on the mechanical and barrier properties of cast biopolymer films

V. Jost and C. Stramm, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42513](https://doi.org/10.1002/app.42513)

The effect of oxidized ferulic acid on physicochemical properties of bitter vetch (*Vicia ervilia*) protein-based films

A. Arabestani, M. Kadivar, M. Shahedi, S. A. H. Goli and R. Porta, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42894](https://doi.org/10.1002/app.42894)

Effect of hydrochloric acid on the properties of biodegradable packaging materials of carboxymethylcellulose/poly(vinyl alcohol) blends

M. D. H. Rashid, M. D. S. Rahaman, S. E. Kabir and M. A. Khan, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42870](https://doi.org/10.1002/app.42870)



Hybrid carrageenan-based formulations for edible film preparation: Benchmarking with kappa carrageenan

Fabio D. S. Larotonda,^{1*} María D. Torres,^{2,3} Maria P. Gonçalves,¹ Alberto M. Sereno,¹ Loic Hilliou^{1,2}

¹REQUIMTE/LAQV, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal

²IN, Institute for Nanostructures, Nanomodelling and Nanofabrication, University of Minho, Campus de Azurem, 4800-058 Guimaraes, Portugal

³Department of Chemical Engineering, University of Santiago de Compostela, Lope Gómez de Marzoa St, Santiago de Compostela 15782, Spain

*Present address: Ministry of Science, Technology and Innovation, Esplanada dos Ministérios, Bloco E, 70067-900, Brasília-DF, Brazil

Correspondence to: L. Hilliou (E-mail: loic@dep.uminho.pt)

ABSTRACT: An intense search for new renewable sources to produce natural polymers for edible and biodegradable packaging is observed as they offer lower environmental costs. The objective of this work is to investigate the use of hybrid carrageenan, extracted from *Mastocarpus stellatus* seaweeds, as an alternative to commercial kappa carrageenan in new edible film formulations. To this end, the production and characterization of biodegradable films obtained with mixtures of rice starch and hybrid carrageenan or commercial kappa carrageenan were carried out. Thin, flexible, and transparent films with attractive functional properties were obtained from rice starch–carrageenan mixtures. Films forming solutions produced with hybrid carrageenan showed rheological properties comparable to commercial kappa carrageenan-based solutions. Films formulated with hybrid carrageenan show significantly enhanced UV barrier, oxygen barrier, and hydrophobic properties. Thus, hybrid carrageenan proved to be a promising material for the production of edible coatings and biodegradable films and a good alternative to kappa carrageenan for such application. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42263.

KEYWORDS: films; morphology; polysaccharides; rheology; structure; property relations

Received 30 October 2014; accepted 23 March 2015

DOI: 10.1002/app.42263

INTRODUCTION

The search of environment-friendly and biodegradable polymers for food applications has gained a notable interest in recent years as a result of increased worldwide concern about sustainability issues. The problems of overflowing landfills, polluted marine waters and plastics waste have accelerated the need to develop biodegradable and biosourced polymers. Food packaging has become a central focus of waste reduction efforts. Packaging protects food from its environment. Quality and shelf life are reduced when food, through interaction with its environment, gains, or loses moisture or aroma, takes up oxygen (leading to oxidative rancidity), or becomes contaminated with microorganisms. In multicomponent foods, quality and shelf life are also reduced when moisture, aromas, or lipid migrate from one food component to another.¹ Petroleum-derived plastic materials are extensively used for food-packaging today because of their availability in large quantities at low cost and favorable functional attributes. More alternative packaging materials based on renewable resources have to be found to

avoid problems concerning sustainability and waste disposal.² Thus, the search for biodegradable packaging films has recently boosted.^{3–7}

In this context, edible natural polymers are a specific type of ecofriendly alternative to petroleum-based polymers. Although edible films are not meant to totally replace synthetic packaging films, they have the potential to reduce packaging.¹ Indeed, edible films can be used as a vehicle for incorporating natural or chemical antimicrobial agents, antioxidants, enzymes, or functional ingredients.^{5–8} Thus, an edible film coating the food can contribute to the design of new plastic packages requiring less petroleum-based polymers, or even pack efficiently the food. The functional characteristics required for the edible coatings and films depend on the product matrix (low to high moisture content) and the deterioration processes the product is subjected to.^{4–10} Edible films can be made of renewable materials, such as polysaccharides and proteins. These film materials are characterized by high moisture permeability, low oxygen, and lipid permeability at lower relative humidity. However, they

show compromised barrier and mechanical properties at high relative humidity.¹¹

Films made from different types of polysaccharides display a wide range of properties,¹² as a result of the wide range of chemical structures and film forming behavior. Starch is an increasingly interesting natural material for the production of edible films because it is quite cheap, abundant, biodegradable, and edible.¹³ Edible films made from starch appear to have moderate oxygen barrier properties, but are poor moisture barriers. Their mechanical properties are generally inferior to synthetic polymers.¹ Improvement of films functional properties may be achieved by blending starch with another natural edible biopolymer with good film forming properties. Carrageenans are water-soluble natural polymers extracted from red seaweed, and are extensively used in food and pharmaceutical industries as gelling and stabilizing agents. The gelling ability of kappa and iota carrageenans imparts excellent film forming properties.¹⁴ Coatings that include carrageenan have been applied to a variety of foods to carry antimicrobials and to reduce moisture loss, oxidation, or disintegration.¹ The addition of carrageenan to starch-based systems results in several physical effects which are now well documented. Carrageenan can equally act as a starch solution thickener, a gel-accelerating or gel-retarding agent, a gel-strengthening or gel-weakening agent, depending on the polysaccharide type.¹⁵ However, little is known about the effect of carrageenan on the ultimate properties of film cast from carrageenan–starch mixtures,¹⁶ and nearly all studies relied on the use of commercial carrageenan grades with gelling properties.

In a previous work,¹⁷ a set of hybrid carrageenans isolated from *Mastocarpus stellatus* seaweeds showed different gelling properties depending on the extraction parameters used to recover the biopolymers. This type of carrageenan can be seen as a statistical copolymer made of blocks of iota carrageenan, blocks of kappa carrageenan, and other nongelling carrageenan monomers.¹⁸ As a result of this specific chemical structure, hybrid carrageenans exhibit gelling properties which are intermediate between those of pure iota carrageenan and pure kappa carrageenan gels.^{19,20} Therefore, hybrid carrageenans have recently received an increased interest for specific food applications such as dairy,^{19,21} but also for replacing carrageenan mixtures in other applications. This is because carrageenan market puts a lot of pressure on the natural resource²² whereas hybrid carrageenan is extracted from less exploited seaweeds. However, the film forming properties of hybrid carrageenans have attracted to date little attention. These properties were first tested for knife coating application and for the edible coating of fruit, achieving promising results with the enhancement of the fruit shelf life due to a reduced water loss.²³ The functional properties of the hybrid carrageenan were then ameliorated by plasticizing or reinforcing with mica^{24,25} or cellulose nanowhiskers.²⁶ These novel hybrid carrageenan-based biocomposites showed better mechanical properties in terms of elasticity, and enhanced barrier properties to water when compared to hybrid carrageenan films. In addition, a detailed study on the morphology and water barrier properties of the nanobiocomposites produced with cellulose nanowhiskers showed that despite the nano-

whiskers agglomeration occurring at larger loading, biobased nanoreinforced carrageenan could be produced with attractive barrier properties.²⁶ Nevertheless, the question arises whether such results are specific to hybrid carrageenan and whether equivalent barrier properties can be achieved by blending with a semicrystalline natural polymer, instead of mixing with nanofillers.

Here, we report the comparative study of two series of films obtained from cast and dried solutions of rice starch mixed with hybrid carrageenans obtained from *M. stellatus* or mixed with a commercial kappa carrageenan. The main objective of this study is to benchmark the properties of films made from hybrid carrageenan with those of films made with commercial kappa carrageenan, as the hybrid carrageenan is essentially made of kappa carrageenan blocks (see below). Films functional properties relevant for edible film application are extensively studied. The paper starts with a section reporting the rheological properties of the film forming solutions. This section is followed by the presentation of microstructural properties of films as well as their water sorption attributes. Then, all functional properties are presented and discussed in light of the rheology, microstructural and water sorption data.

EXPERIMENTAL

Raw Materials

Rice starch (Sigma-Aldrich) and kappa carrageenan (SKW Biosystems, France) were used as received to produce the film forming solutions. Both ¹H-NMR and ¹³C-NMR analyses confirmed that this commercial carrageenan product is essentially a kappa carrageenan homopolymer. However, characteristic peaks at 74.34 and 5.36 ppm for ¹³C-NMR and ¹H-NMR spectra respectively, indicate the presence of roughly 10 mol % of Floridian starch.²⁷ Hybrid carrageenan was isolated from *M. stellatus* using an extraction process optimized with respect to both biopolymer yield and gel properties, as described in length elsewhere.^{17,18,23} This natural biopolymer consists in roughly 50 mol % kappa carrageenan, 30 mol % iota carrageenan, and 20 mol % nongelling carrageenan disaccharide units. Elemental analysis with inductively coupled plasma optical emission spectrometry (Jobin Yvon Ultima, Edison, NJ) showed that the recovered product contains 3 wt % sodium salt resulting from the alkaline treatment of seaweeds used prior to biopolymer extraction in order to enhance the gel elasticity.

Film Preparation

Carrageenan–starch aqueous mixtures, with different amount of carrageenan (16.7, 33.3, 44.4, and 100 wt % in film dry basis) were prepared at least in triplicate with a 4 wt % total biopolymer concentration in distilled water. The mixtures with commercial kappa carrageenan were codified as KAPPA and the mixtures with hybrid carrageenan extracted from *Mastocarpus stellatus* were codified as HYBRID. Required weights of carrageenan and starch were added to hot distilled water. The aqueous mixtures were heated at 80°C under stirring during 30 min for achieving complete solubility of starch and carrageenan. The mixture was spread over a Teflon® plate and dried at room temperature to form the film within 2 days. Specifically, in order to obtain a A4 size film, 150 mL of film forming solution was cast

on a 300 mm long and 250 mm wide Teflon[®] plate. All the films were easily removed from the Teflon[®] plate and showed smooth surfaces. Homogeneous, thin, flexible and transparent films were obtained from all carrageenan-starch mixtures reported here. The thickness of film samples was measured at four different points using a manual micrometer (Mitutoyo) giving a mean value of $50 \pm 5 \mu\text{m}$. It should be mentioned here that films formed from pure rice aqueous solutions were very brittle and fragile. Thus, no mechanical testing could be performed as films broke during loading. Similarly, water and oxygen permeability could not be performed with pure rice starch films as samples simply broke upon loading in the permeability cells or during testing (see below).

Rheology of Film Forming Solutions

Prior to film casting, a sample of the hot film forming solution was loaded between the preheated (at 90°C) parallel plates of a stress-controlled rheometer (AR2000, TA Instruments). Right after loading, the shearing geometry was covered with paraffin oil to prevent any water loss and 10 min were left to the sample to equilibrate at 90°C . Then the samples were cooled ($-5^\circ\text{C}/\text{min}$) down to 20°C and thermal and structural equilibrium at this temperature was monitored by small amplitude oscillatory shear (SAOS) performed at 1 Hz and a strain of 1%. When SAOS data reached a constant reading for both storage (G') and loss moduli (G''), a frequency sweep was recorded with a strain of 1%. These measurements were performed at least in duplicate for each studied solution.

Water Sorption Isotherms

Water sorption isotherms were determined at least in duplicate for each sample at 25°C by the gravimetric method, following the procedure reported elsewhere.²⁸ The Guggenheim–Andersode Boer (GAB) model²⁹ was used to represent the experimental sorption data. In this model, the equilibrium moisture content X at a given water activity a_w is

$$X = \frac{CkX_0a_w}{[(1-ka_w)(1-ka_w + Cka_w)]} \quad (1)$$

where X_0 is the monolayer moisture content and represents the water content corresponding to saturation of all primary adsorption sites by one water molecule, C is the Guggenheim constant and represents the energy difference between the water molecules attached to primary sorption sites and those absorbed to successive sorption layers, and k is the corrective constant taking into account properties of multilayer molecules with respect to the bulk liquid. GAB equation parameters were calculated from fits of equation (1) to experimental data (see Figure 4), using STATISTICA software version 6.0 (Statsoft).

Mechanical Properties

The films tensile properties were studied using a TAXT2 Stable Micro Systems texture analyzer (Surrey, UK) in accordance with ASTM D-882-91. Five sample strips ($25 \times 100 \text{ mm}^2$) of each formulation were cut and clamped between grips. Force and distance were recorded during extension performed at a rate of 0.2 mm/s and with an initial distance between the grips of 60 mm. The parameters determined were: stress at break Σ ,

strain at break ε_b and Young's modulus E . The samples were conditioned at a relative humidity of 53% for a week before performing the mechanical assays.

Water Vapor Permeability (WVP)

WVP tests were conducted at least in triplicate for each film using ASTM method E96-95 with some modifications. Each film sample was sealed over a circular opening 0.003 m^2 in a permeation cell that was stored at 25°C in a desiccator. The driving force, expressed as water vapor partial pressure, was 3106.51 Pa . To maintain this driving force corresponding to a 98% relative humidity (RH) gradient across the film, anhydrous calcium chloride (2% RH) was used inside the cell and distilled water (100% RH) was used in the desiccator. A fan was operated within the chamber to avoid the stagnant air. The test cell was periodically weighted after steady state conditions were reached (after about 2 h, a constant weight variation rate was observed). WVP ($\text{g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$) was calculated using the following equation:

$$\text{WVP} = \frac{\Delta m \cdot x}{A \cdot \Delta t \cdot \Delta p} \quad (2)$$

where Δm is the weight gain of the test cell, x is the film thickness, and A is the exposed area (0.003 m^2) during duration Δt under a partial water vapor pressure Δp .

Oxygen Permeability

Oxygen transmission rate was determined at least in triplicate for each film using a homemade static diffusion cell.³⁰ Discs with 90 mm diameter were cut from the sample film and conditioned for 7 days at room temperature and under a controlled relative humidity of 53%. Discs were then sealed on the circular aperture of the static diffusion cell and a purging gas (Helium) circulated through the cell compartment which is separated from the atmosphere by the sample film and is equipped with a gas sampling port. When no oxygen can be detected in the gas samples collected through the cell port and analyzed with a CheckMate II gas analyzer (PBI Dansensor, Denmark), all valves are closed and permeability test is started. At given time intervals, small gas samples are taken from the cell and oxygen concentration is measured with the gas analyzer. The oxygen transmission rate OTR is then computed from the slope of the time dependence of the amount of oxygen that permeated through the film. Oxygen permeability OP is then calculated using the following relationship:

$$OP = \frac{OTR \cdot x}{A \cdot \Delta p} \quad (3)$$

where x is the film thickness, A the exposed film area, and Δp is the difference in oxygen partial pressure between atmospheric air and cell compartment.

Optical and Light Barrier Properties

Film color was determined with a Minolta CR300 series (Tokyo, Japan), and the CIELab color parameters, namely lightness L^* and chromacity parameters a^* (red–green) and b^* (yellow–blue), were measured. The color of the films was expressed as

the difference of color ΔE^* , computed from the following equation:

$$\Delta E^* = \sqrt{(L^* - L_s^*)^2 + (a^* - a_s^*)^2 + (b^* - b_s^*)^2} \quad (4)$$

where L_s^* , a_s^* , and b_s^* are the CIELab color parameters of the white standard used as the film background. The ultraviolet (UV) and visible light barrier properties of films were determined by measuring films absorbance A_x at wavelengths x ranging from 200 to 600 nm using a UV–visible spectrometer (Unicam Helios alpha, Cambridge, UK). Samples (1×2 cm) with identical thickness (to the limit of resolution, 1 μm , of the micrometer) were cut from films equilibrated at a relative humidity of 53% for 1 week, then sandwiched between two optical microscopy slabs and inserted in the optical path of the spectrophotometer. The sandwiched samples were then immediately imaged with crossed polarizer and analyzer using a Olympus BH2 optical microscope. These measurements were made at least in triplicate for each film.

Dielectric Spectroscopy

Dielectric spectroscopy measurements were carried out at the Max Planck Institute for Polymer Research, Germany, using a Novocontrol Dielectric Broadband Spectroscopy. The dielectric constant (ϵ') and loss factor (ϵ'') were measured at 25°C in a frequency range of 10^{-3} to 10^7 Hz. The experiments were performed at least in duplicate with the samples equilibrated at room conditions (25°C; 58%RH).

Statistical Analysis

A one-way analysis of variance (ANOVA) was performed using STATISTICA software (StatSoft) version 6.0, in order to test for significant (the significance level was 0.05) differences between films properties.

RESULTS AND DISCUSSION

Rheology of Film Forming Solutions

Figure 1 shows the frequency dependence of the storage (G') and loss (G'') moduli of film forming solutions prepared with a total concentration of 4 wt % of polysaccharide in distilled water. The commercial carrageenan exhibits a mechanical spectrum characterized by large moduli with weak frequency dependence for the whole range of tested frequencies. This is reminiscent from a highly entangled polymer solution, or a weak gel³¹ with large elasticity but weak rigidity as G'' is only two to three times smaller than G' . In contrast to this, the mechanical spectrum of the hybrid carrageenan displays the characteristics of a gel slightly above its gel point. The low frequency regime shows an elastic behavior (G' is constant and significantly larger than G''), whereas both moduli show a similar asymptotic behavior at larger frequencies. The mechanical spectrum of the rice starch sample shows the features of a hydrogel with weak elasticity which is indicative of starch retrogradation upon cooling.³² Mixing carrageenan and starch results in a drastic change in the rheological characteristics of the film forming solutions. The mechanical spectrum of an aqueous mixture where 10% commercial carrageenan is replaced by rice

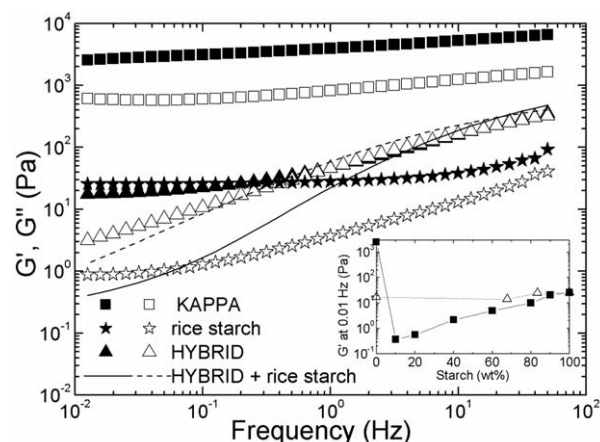


Figure 1. Mechanical spectra (G' : solid symbols; G'' : open symbols) of film forming solutions with 4 wt % total polysaccharide concentration in distilled water at 20°C: KAPPA (squares), rice starch (stars), HYBRID (triangles), and a mixture of KAPPA (3.6 wt %) with 0.4 wt % rice starch (G' : solid line; G'' : dashed line). Inset: evolution of the storage modulus G' measured at 0.01 Hz and 20°C of mixtures as a function of the rice starch content in wt % in the final dried film.

starch indicates that the film forming solution is essentially a viscoelastic liquid at 20°C, as G'' is larger than G' for the whole frequency range tested. Thus, a small dilution of commercial carrageenan by starch solution is sufficient to impede the percolation of the three dimensional carrageenan network. This dilution transforms the gel into a viscoelastic liquid. A gel behavior is recovered when more than 60% rice starch is added to the film forming solution (results reported elsewhere).³⁰ Thus, the dependence of the storage modulus measured at 0.01 Hz on the rice starch amount in the mixture (see inset to Figure 1) does not show the monotonic behavior of ideal mixtures as phase transition from liquid to gel occurs with increasing amount of rice starch. This is indicative of a phase separation between starch and carrageenan, and as such this behavior is in agreement with the one reported for blends of starch with different galactomannans.³³ Similar rheological patterns (not shown) were obtained for mixtures with hybrid carrageenan prepared with more than 60% rice starch. As such, values of G' in the inset of Figure 1 are very close to the values measured with commercial carrageenan, as the network formed by rice starch essentially rules the elasticity in the mixture. As data in Figure 1 show that commercial carrageenan forms a much more elastic gel than hybrid carrageenan for a similar polysaccharide concentration, we may expect that upon the drying of film forming solutions, a phase separated or an interpenetrated network may develop with hybrid carrageenan forming a weaker network with less connectivity or cross linking density than the commercial carrageenan. This should result in different film morphologies since starch crystallization upon drying will be affected by the buildup and the structuration of the carrageenan network.

Films Microstructure and Optical Properties

The films cast from film forming solutions are very sensible to water, as they dissolve in cold distilled water within 10 min. Figure 2 presents polarized optical micrographs of a HYBRID

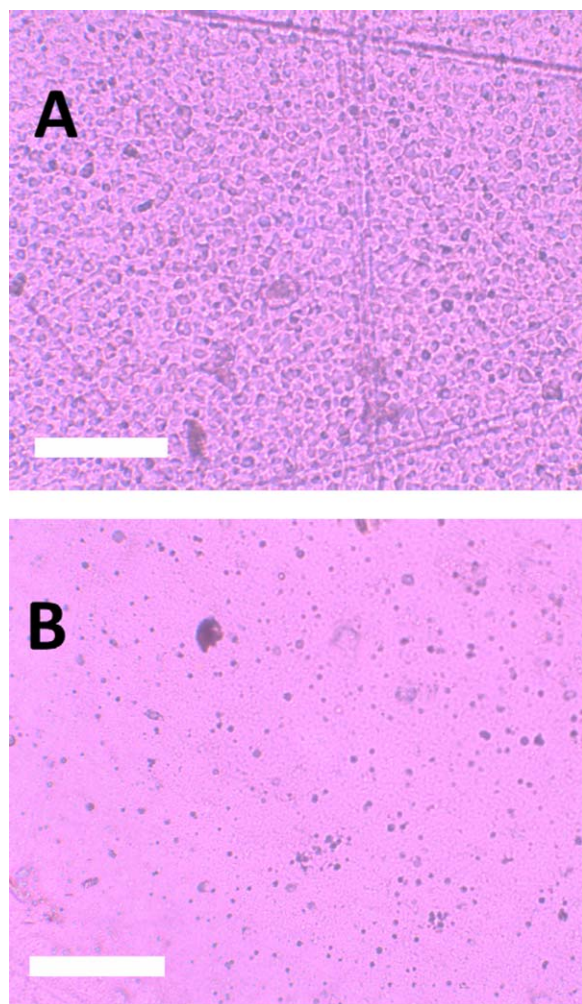


Figure 2. Polarized optical microscopy images of HYBRID (A) and KAPPA (B) films obtained with 55.6 wt % rice starch. White horizontal bars in images indicate 10 μm . Lines in the pictures correspond to surface defects from the casting mould. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

film and a KAPPA film obtained with identical formulation (44.4 wt % carrageenan). Starch granules are clearly evidenced in the HYBRID film (moisture content of 0.11 g/g) and are larger than the granules observed in the KAPPA film (moisture content of 0.16 g/g). Both microstructures conform to the phase separation established by the rheological results. Similar film morphologies were recently reported for carrageenan–starch mixtures.¹⁴ The morphological difference could be related to the rheological evidence for a stronger (and thus more connected) carrageenan network reported above for the commercial kappa carrageenan: rice starch crystals are more confined by the carrageenan network, and thus smaller crystals develop. It has been recently suggested that differences in the water content in respective films could also tune the starch crystallinity.^{34,35} The crystallinity of starch films is very sensitive to water content since starch crystallizes during drying but also to the gelatinization temperature used to prepare the films. Here the temperature was 80°C, and according to Ref. 35, at this temperature the crystallinity index is about 40% for all film forming

solutions. However, final water content in films could be different and also contribute to different crystallinities and crystal sizes.

Color standards parameters of all films are presented in Table I. KAPPA films are colorless whereas HYBRID ones show a slightly yellow appearance, as no bleaching treatment was used during the extraction of the hybrid carrageenan. The yellow appearance of HYBRID films is mirrored in both b^* and ΔE^* parameters which increase with the increased content in hybrid carrageenan. All the colors parameters (L^* , a^* , and b^*) differ significantly ($F = 423.98$, $P = 0$; $F = 213.68$, $P = 3.33E-16$; $F = 728.50$, $P = 0$; respectively for L^* , a^* , and b^*) for all film formulation. The absorbance of representative films is displayed in Figure 3. The addition of carrageenan essentially improves the UV barrier properties of starch-based films as both HYBRID and KAPPA films present larger absorbance in the range 200–300 nm. This result suggests that these films can efficiently prevent lipid oxidation induced by UV light. If good UV barrier properties are desired while keeping good transparent properties in the visible range, then HYBRID films are the material of choice. They perform better than KAPPA films in the UV range while preserving as good transparency as KAPPA in the range of 600 nm which is the usually referred wavelength for such optical asset.³⁴

Water Sorption Isotherms

Moisture sorption isotherms at 25°C for KAPPA and HYBRID films are presented in Figure 4, together with the GAB model [see eq. (1)] fit to each data set. The GAB equation parameters are gathered in Table II. The values of parameter k (all smaller than 1) and of the correlation coefficients r (also collected in Table II) show that the GAB model gives a satisfactory fit to experimental data. Because of their hydrophilic nature, hydrocolloid film properties are highly dependent on environmental conditions such as relative humidity and temperature.^{10,36,37} An important quantity of water can be held within the film structure. The isotherms curves in Figure 4 present a sigmoidal shape. This indicates that the equilibrium moisture content increases slowly with increasing environmental a_w up to 0.7. At larger a_w , a steep rise in the moisture content in film samples was observed. The pure rice starch film exhibits a less hygroscopic behavior, as the moisture content measured for all water activities is the lowest of all studied films. Rice starch film shows higher monolayer moisture content X_0 than other film samples (see Table II), and X_0 values suggest that the monolayer moisture content is specific to the chemical nature of the film-forming substance. The main output from moisture sorption isotherms is summarized in Figure 5 for clarity, where X measured at 2 different a_w are plotted against the rice starch content in the film. Addition of rice starch in film formulation results in decreased hydrophilic properties of the films, which is expected if one considers the higher hydrophobic character of starch as inferred from data obtained with pure starch or pure carrageenan films. The use of hybrid carrageenan extracted from *M. stellatus* significantly reduces the hygroscopic behavior of the films, as films made from commercial kappa carrageenan show greater moisture content for all compositions tested.

Table I. Colors Standards of Films with Different Kappa Carrageenan (KAPPA) or Hybrid Carrageenan (HYBRID) Compositions

Film	L^*	a^*	B^*	ΔE^*
Rice Starch (100%)	99.37 ^a ± 0.08	0.57 ^a ± 0.03	2.05 ^a ± 0.02	0.05 ^a ± 0.31
KAPPA (83.3%)	99.34 ^a ± 0.07	0.59 ^a ± 0.04	2.62 ^{ac} ± 0.16	0.59 ^b ± 0.32
KAPPA (66.7%)	98.49 ^b ± 0.11	0.44 ^a ± 0.05	4.31 ^b ± 0.35	2.44 ^d ± 0.49
KAPPA (55.6%)	99.09 ^a ± 0.13	0.50 ^a ± 0.05	3.61 ^{bd} ± 0.21	1.60 ^{c,d} ± 0.46
KAPPA (0%)	98.97 ^{ab} ± 0.12	0.57 ^a ± 0.02	3.11 ^{cd} ± 0.20	1.14 ^c ± 0.34
HYBRID (83.3%)	97.91 ^c ± 0.32	0.26 ^b ± 0.04	5.31 ^e ± 0.37	3.60 ^d ± 0.50
HYBRID (66.7%)	95.73 ^d ± 0.33	0.00 ^c ± 0.04	9.37 ^f ± 0.12	8.20 ^e ± 0.15
HYBRID (55.6%)	93.87 ^e ± 0.24	-0.35 ^d ± 0.04	12.79 ^g ± 0.41	12.11 ^f ± 0.33
HYBRID (0%)	93.77 ^e ± 0.13	-0.40 ^d ± 0.08	12.72 ^g ± 0.35	12.10 ^f ± 0.54

Numbers between parentheses in first column indicate the amount (in wt % dry weight of film) of rice starch.

Data are presented as mean ± standard deviation. Data values in a column with different superscript letters are significantly different at the $P \leq 0.05$ level.

Dielectric Spectroscopy

The dielectric constant (permittivity ϵ') of film is usually related to the film polarity and relaxation processes of dipolar moments in the film. Scarce information is available in the literature on the dielectric properties of polysaccharide-based films, however the curves displayed in Figure 6 show qualitative similarities with dielectric spectra reported for gelatin-based films and maize starch-based films.^{38,39} Overall, the results presented in Figure 6 show that ϵ' of starch-carrageenan films is much lower than that of semisolid or liquid biological samples due to the relatively lower water content and limited mobility of the polymer molecules in the films, but is the same order of magnitude to that of common synthetic films. Films with more carrageenan exhibited larger ϵ' values than rice starch films for the whole range of tested frequencies. However, two carrageenan films show an opposite behavior at larger frequencies. As shown above, carrageenan is more hygroscopic than starch and adsorbs more water (see Figure 3). Water is polar and also acts as a plasticizer of the film. Thus, the addition of carrageenan leads to an increase in water content, facilitating the mobility of the

polar groups and enhancing dipole orientation in the film.³⁹ These outcomes showed that dielectric constant of the studied films is highly related to their water content, which is consistent with the results found in a relevant study on the dielectric properties of konjac glucomannan films.⁴⁰

Films Mechanical Properties

The tensile properties of the starch-carrageenan films are presented in Figure 7 as a function of the rice starch content in the films. Both Young modulus E and strain at break ϵ_b displayed by films made of hybrid carrageenan differ significantly from values obtained with kappa carrageenan-based films ($F = 10.96$, $P = 2.29E-5$, and $F = 12.21$, $P = 1.08E-5$, respectively, for E and ϵ_b). A similar conclusion is drawn for the stress at break Σ ($F = 25.57$, $P = 4.07E-8$). The impact of carrageenan chemistry on carrageenan film mechanical properties is in harmony with data recently reported⁴⁰ for films made of carrageenans extracted from *Eucheuma* species seaweeds. The stress at break, the tear strength and the Young modulus of kappa-carrageenan films were found to be significantly larger than those of iota-carrageenan films. To explore whether the water content in films

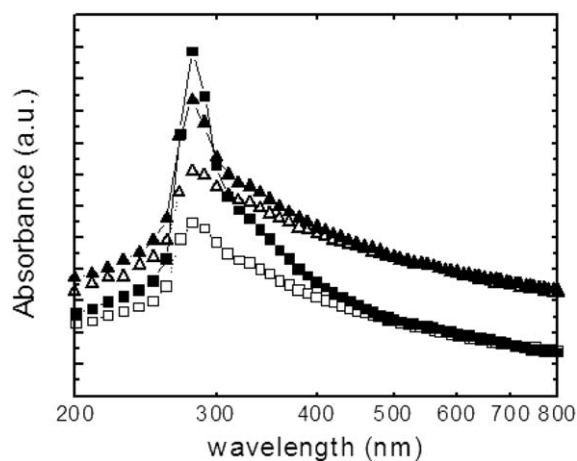


Figure 3. Light transmission spectra (absorbance) of carrageenan-based films with different contents in rice starch (solid symbols: 66.7 wt %; open symbols: 83.3 wt %) and type of carrageenan (HYBRID: squares; KAPPA: triangles).

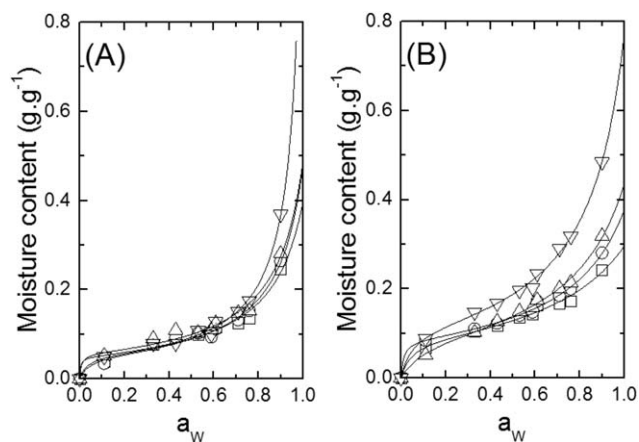


Figure 4. Moisture content X (on dry film basis) as a function of the water activity a_w for HYBRID films (a) and KAPPA films (b) containing 83.3 wt % (squares), 66.7 wt % (circles), 55.6 wt % (up triangles) or 0 wt % (down triangles) rice starch. Lines are fits of eq. (1) to the data.

Table II. Parameters of the GAB Model Obtained from the Fit of Equation (1) to the Water Sorption Data Plotted in Figure 1

Film	X_0 ($g\ g^{-1}$)	C	K	R
Rice starch (100%)	1.7716	29.6395	0.0049	0.9687
KAPPA (83.3%)	0.0882	29.9782	0.7058	0.9943
KAPPA (66.7%)	0.0839	113.6263	0.7783	0.9971
KAPPA (55.6%)	0.0955	11.3395	0.7863	0.9985
KAPPA (0%)	0.1136	23.3199	0.8544	0.9986
HYBRID (83.3%)	0.0527	34.9089	0.8683	0.9889
HYBRID (66.7%)	0.0517	24.8645	0.8931	0.9926
HYBRID (55.6%)	0.0559	151.5160	0.8858	0.9901
HYBRID (0%)	0.0483	261.2258	0.9653	0.9972

r is the correlation coefficient computed from the fit of equation (1) to the data. Numbers between parentheses in first column indicate the amount (in wt % dry weight of film) of rice starch.

rather than the different chemical carrageenan structure explains the difference in films mechanical properties, the inset in Figure 7 presents the Young moduli of films as a function of their water content. This plot indicates that two KAPPA-based films showing significantly larger water contents exhibit Young moduli equivalent to those exhibited by HYBRID-based films. Figure 7 also shows that E is a decreasing function of the content in rice starch in HYBRID films, which in turn contain less water. Thus, the well-known plasticizing effect of water cannot explain these results. In contrast to this, KAPPA films show an increasing Young modulus with increasing rice starch content. This relates to the decrease in water content of the films. However, above 66.7% rice starch, the Young modulus of KAPPA-based films drops. Therefore, the mechanical properties of films result from a complex interplay between water plasticization, polysaccharide chemistry and film microstructure. When cooling the film forming solutions from 80°C, temperature at which carrageenan is in the coil conformation and thus is most probably well assembled with the gelatinized starch, KAPPA and HYBRID undergo a coil-to-helix transition which affect their assembly with starch. Because KAPPA and HYBRID have different carra-

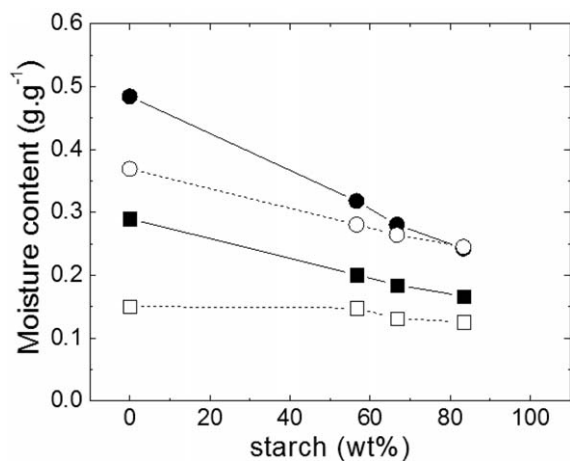


Figure 5. Moisture content X (on a dry film weight basis), for water activities of 0.71 (squares) and 0.90 (circles), as a function of the rice starch content for HYBRID (open symbols) and KAPPA (solid symbols) films.

geenan composition, their respective coil-to-helix transitions occur at different temperature, and they dissociation from retrograding starch is different. Thus, KAPPA and HYBRID phase

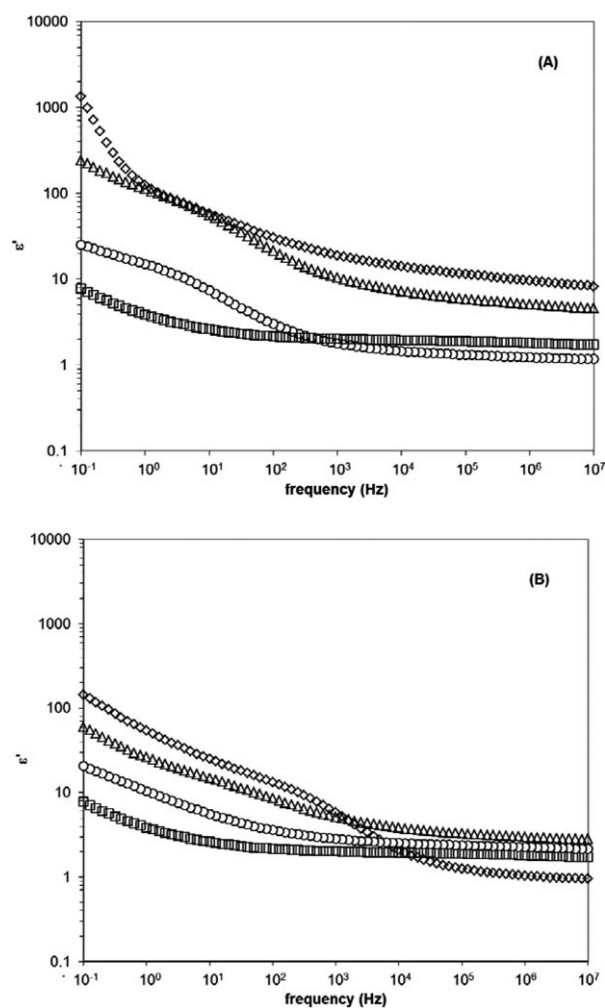


Figure 6. Dielectric constant (ϵ' —permittivity) at 25°C of carrageenan-based films as a function of frequency at different amount of rice starch in the mixture [100 (stars), 83.3 (circles), 55.6 (triangles), and 0 (diamonds) %]—(A) commercial kappa carrageenan (KAPPA); (B) hybrid carrageenan (HYBRID).

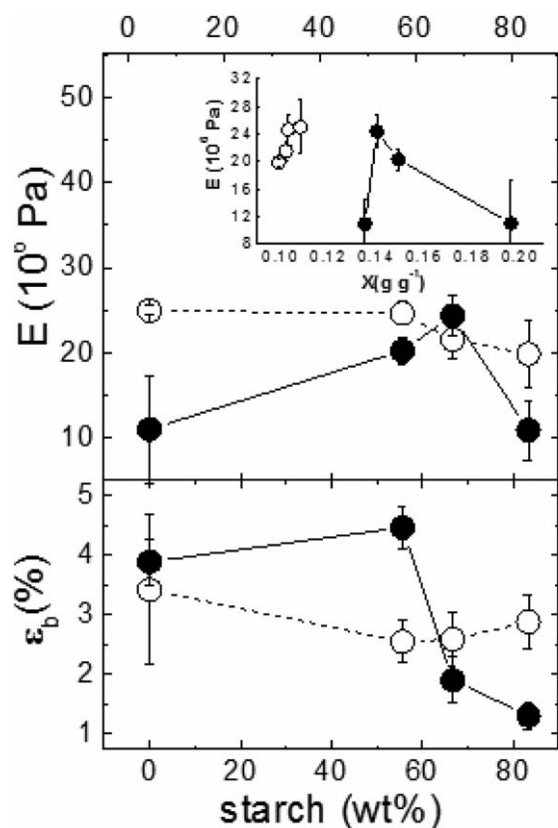


Figure 7. Tensile properties as a function of rice starch content for HYBRID (open symbols) and KAPPA (solid symbols) films. Inset: evolution of the Young modulus as a function of moisture content for all films produced.

separate from the retrograded starch, but the extent of phase separation is different, as suggested by the different rheological characteristics of film forming solutions at 20°C (see Figure 1). Upon drying, the extent of phase separation evolves and the starch–carrageenan assembly is further changed. Indeed, Figure 2 shows a characteristic phase separated structure where starch grains are dispersed in a carrageenan matrix. We can thus argue that the nonmonotonic variation of film mechanical properties with increasing starch content is reminiscent from phase inver-

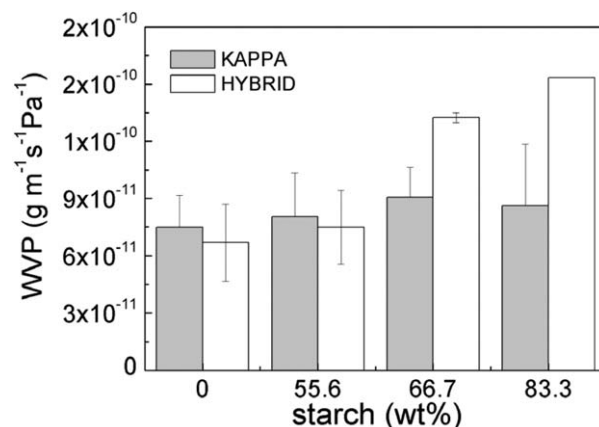


Figure 8. Water vapor permeability of HYBRID and KAPPA starch–carrageenan films as a function of film compositions.

sion phenomena in the film state.³⁹ Below phase inversion, starch crystals reinforce the carrageenan matrix and Young moduli are improved. Note here that such effect implies good interface between starch crystals and carrageenan matrix, which in turn indicates residual good assembly between these two components. Above phase inversion, the picture is changed as starch rules the mechanical properties. Table III provides a comparison of KAPPA and HYBRID film mechanical properties with those of conventional packaging materials and of edible films recently studied in the literature. Starch–carrageenan films showed comparable mechanical properties as those obtained with chitosan, corn starch, or whey proteins.

Water Vapor Permeability

The water vapor permeability of starch–carrageenan films is displayed in Figure 8. The addition of rice starch to commercial kappa carrageenan does not significantly ($F = 0.27$; $P = 0.88$) affect the permeability of KAPPA films as WVP values virtually level off at $9 \times 10^{-11} g s^{-1} m^{-1} Pa^{-1}$ for all compositions. Conversely, the water vapor permeability of HYBRID films shows a significant ($F = 12.94$; $P = 0.02$) increase with the addition of rice starch. The contrast between the WVP properties of KAPPA and HYBRID films suggests that film morphology, and in particular rice starch crystals are related to WVP: for all

Table III. Comparison of KAPPA and HYBRID Films Functional Properties with Similar Properties Reported for Films Made of Natural Polymers or Synthetic Polymers Used in Food Packaging

Film	Test conditions	WVP ($\times 10^{-11}$ $g m^{-1} Pa^{-1} s^{-1}$)	OP ($\times 10^{-12}$ $cm^3 m^{-1} Pa^{-1} s^{-1}$)	ϵ_b (%)	Σ (MPa)
KAPPA	25°C, 53% RH	7.5	5.2	3.9	42.5
HYBRID	25°C, 53% RH	6.7	3.3	3.4	55.2
Chitosan	25°C, 93% RH	4.5 ⁽⁴⁷⁾	10.4 ⁽⁹⁾	3.3 ⁽⁴⁷⁾	60.7 ⁽⁴⁷⁾
Whey protein	23°C, 75% RH	1380 ⁽⁴⁸⁾	1.7 ⁽⁴⁵⁾	20 ⁽⁴⁸⁾	2.2 ⁽⁴⁸⁾
Corn starch	24°C, –	18 ⁽⁴⁸⁾	0.15 ⁽⁴⁴⁾	3.6 ⁽⁴⁷⁾	47.4 ⁽⁴⁷⁾
LDPE	23°C, 50% RH	0.091 ⁽⁵⁰⁾	21.6 ⁽⁵¹⁾	68.7 ⁽⁵⁰⁾	16.2 ⁽⁵⁰⁾
HDPE	23°C, 50% RH	0.023 ⁽⁵⁰⁾	4.9 ⁽⁵¹⁾	150 ⁽⁵⁰⁾	27.8 ⁽⁵⁰⁾
Cellophane	23°C, 95% RH	8.4 ⁽⁵¹⁾	2.9 ⁽⁵³⁾	14.4 ⁽⁵²⁾	85.8 ⁽⁵²⁾

Numbers in parenthesis are references to the literature.

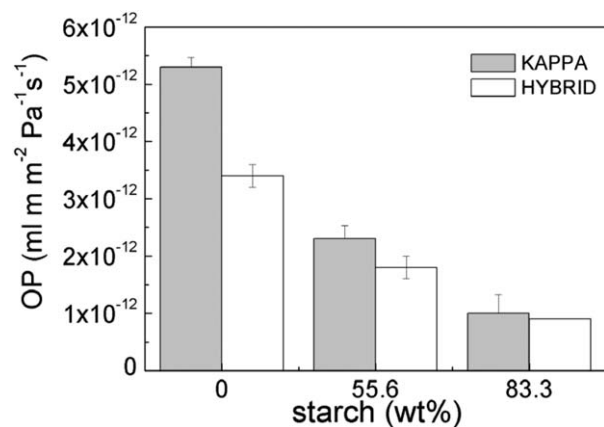


Figure 9. Oxygen permeability (OP) of selected HYBRID and KAPPA films.

compositions, KAPPA films show smaller crystals and thus offer an improved tortuosity for water molecules permeating the film.²⁶ Hydrocolloid films are usually characterized by their good gas barrier properties but poor water vapor permeabilities.^{1,41–43} Compiled WVP data in Table III indicate that KAPPA and HYBRID films show WVP values similar to most of films made from natural polymers, with the exception of whey protein which roughly shows a tenfold larger WVP. With respect to synthetic polymers, both KAPPA and HYBRID films perform as good as cellophane, but exhibit much higher WVP than low density polyethylene (LDPE) films, which are the most commonly materials used in the food packaging industry.

Oxygen Permeability

Oxygen permeability (OP) of selected KAPPA and HYBRID films is presented in Figure 9. There is a significant difference ($F = 331.7$; $P = 2 \times 10^{-12}$) between the oxygen barrier properties of the two sets of films. Adding rice starch to commercial kappa carrageenan or hybrid carrageenan allows for a significant reduction in OP. It should be noted that OP of pure rice starch films could not be determined due to the rupture of films before test completion. This bad mechanical resistance is perhaps at the origin of the lack of OP values reported for starch-based films.²⁸ However, data from the literature^{44–49} suggest that the OP of films made from corn starch is 10 times lower than the smallest OP value found in the present study. The decrease in OP achieved upon addition of rice starch is thus related to the high OP values found for pure carrageenan films in comparison to the OP of starch films found in the literature (see Table III). Film plasticization by water provides an explanation for the better OP of KAPPA films. KAPPA films contain relatively more water than HYBRID films for the relative humidity (53%) at which they were conditioned prior to OP testing (see Figure 4). The enhanced macromolecular chain mobility resulting from the plasticizing effect of water favors the oxygen permeation through the film.^{50–52} In addition, starch crystals in HYBRID films are larger and the microstructure evidenced in Figure 2 also suggests that the crystal volume fraction is larger than in KAPPA films. Thus, if one assumes that starch crystals are barriers to OP, more crystals in HYBRID films are at the origin of a better barrier to the oxygen permeation when

compared to KAPPA films. OP data gathered in Table III indicate that both KAPPA and HYBRID films present intermediate oxygen barrier properties between bio-based films and synthetic films. As such, edible films studied here are good candidate for fresh fruit and vegetable preservation applications where moderate oxygen barrier properties are required to allow a controlled respiratory exchange.

CONCLUSIONS

Although hybrid carrageenan solutions showed less elastic gel properties when compared to kappa carrageenan solutions, when more than 50 wt % rice starch is added all film forming solutions showed essentially similar rheological properties. All films presented attractive functional properties. The combined effects of water plasticization and phase separation between carrageenan and starch crystals explain how films properties can be tuned by adding rice starch to carrageenan. A direct consequence of the hydrophilic character of these biodegradable membranes is their relatively high water vapor permeability which compares well with values reported for polysaccharides (methylcellulose and chitosan), and even for cellophane, a synthetic polymer. Oxygen permeability of starch–carrageenan films indicated that these composite materials are good candidates for applications where moderate gas exchange through the film is needed. All starch–carrageenan films show good barrier properties to UV light. The benchmarking of HYBRID films properties with KAPPA films properties demonstrates that HYBRID is the material of choice if one wishes to produce less hygroscopic but more elastic films with better UV and oxygen barrier properties. Further studies are necessary in order to elucidate the chemical reasons for differences between KAPPA and HYBRID films, or to extend the knowledge about the crystalline behaviour to understand why starch does not retrograde in a similar fashion.

ACKNOWLEDGMENTS

This work was supported by the Fundação para a Ciência e a Tecnologia (project POCTI/EQU/45595/2002 and project PEST-C/CTM/LA0025/2013—Strategic Project—LA 25—2013–2014) and by Programa Operacional Regional do Norte (ON.2) through the project “Matepro—Optimizing Materials and Processes”; contract grant number: NORTE-07-0124-FEDER-000037. F.D.S.L. acknowledges the Programme Alβan, the European Union Programme of High Level Scholarships for Latin America, for a scholarship award (E04D027282BR). M.D. Torres acknowledges the financial support (POS-A/2012/116) from Xunta de Galicia’s Consellería de Cultura, Educación e Ordenación Universitaria of Spain and the European Union’s European Social Fund.

REFERENCES

- Krochta, J. M.; De Mulder-Johnston, C. *Food Technol.* **1997**, *51*, 61.
- Weber, C. J.; Haugaard, V.; Festersen, R.; Bertelsen, G. *Food Addit. Contam.* **2002**, *19*, 172.
- Lagarón, J. M. In *Multifunctional and Reinforced Polymers for Food Packaging*; Lagarón, J. M., Ed.; Woodhead Publishing Limited: Cambridge, **2011**; p 1.

4. Jimenez, A.; Fabra, M. J.; Talens, P.; Chiralt, A. *Food Bioprocess Technol.* **2012**, *5*, 2058.
5. Barlow, C. Y.; Morgan, D. C. *Resour. Conserv. Recycl.* **2013**, *78*, 74.
6. Peelman, N.; Ragaert, P.; De Meulenaer, B.; Adons, D.; Peeters, R.; Cardon, L.; Van Impe, F.; Devlieghere, F. *Trends Food Sci. Technol.* **2013**, *32*, 128.
7. Razavi, S. M. A.; Amini, A. M.; Zahedi, Y. *Food Hydrocolloids* **2015**, *43*, 290.
8. Acevedo-Fani, A.; Salvia-Trujillo, L.; Rojas-Grau, M. A.; Martín-Belloso, O. *Food Hydrocolloids* **2015**, *47*, 168.
9. Guilbert, S.; Gontard, N.; Gorris, L. G. M. *Lebensm.-Wiss. Technol.* **1996**, *29*, 10.
10. Debeaufort, F.; Quezada-Gallo, J. A.; Voilley, A. *Crit. Rev. Food Sci. Nutr.* **1998**, *38*, 299.
11. Brody, A. L. *Food Technol.* **2005**, *59*, 65.
12. Nisperos-Carriedo, M. In *Edible Coatings and Films to Improve Food Quality*; Krochta, J. M.; Baldwin, E. A.; Nisperos-Carriedo, M., Eds.; Technomic Publishing: Lancaster, **1994**; p 305.
13. Mali, S.; Grossmann, M. V. E. *J. Agric. Food Chem.* **2003**, *51*, 7005.
14. Park, S. Y.; Lee, B. I.; Jung, S. T.; Park, H. J. *Mater. Res. Bull.* **2001**, *36*, 511.
15. Lai, V. M. F.; Huang, A. L.; Lii, C. Y. *Food Hydrocolloids* **1999**, *13*, 409.
16. Lafargue, D.; Lourdin, D.; Doublier, J. L. *Carbohydr. Polym.* **2007**, *70*, 101.
17. Hilliou, L.; Larotonda, F. D. S.; Abreu, P.; Ramos, A. M.; Sereno, A. M.; Gonçalves, M. P. *Biomol. Eng.* **2006**, *23*, 201.
18. Hilliou, L.; Larotonda, F. D. S.; Sereno, A. M.; Gonçalves, M. P. *J. Agric. Food Chem.* **2006**, *54*, 7870.
19. Hilliou, L.; Gonçalves, M. P. *Int. J. Food Sci. Technol.* **2007**, *42*, 678.
20. Hilliou, L. *Adv. Food Nutr. Res.* **2014**, *72*, 17.
21. Villanueva, R. D.; Mendoza, W. G.; Rodriguez, M. R. C.; Romero, J. B.; Montaña, M. N. E. *Food Hydrocolloids* **2004**, *18*, 283.
22. Bixler, H. J.; Porse, H. J. *J. Appl. Phycol.* **2011**, *23*, 321.
23. Larotonda, F. D. S.; Hilliou, L.; Gonçalves, M. P.; Sereno, A. M. In *Recent Advances in Research on Biodegradable Polymers and Sustainable Composites*, Vol. 3; Jiménez, A.; Zai-ko, G. E., Eds.; Nova Science: New York, **2008**; p 177.
24. Alves, V.; Costa, N.; Hilliou, L.; Larotonda, F.; Gonçalves, M.; Sereno, A.; Coelho, I. *Desalination* **2006**, *199*, 331.
25. Sanchez, M. D.; Hilliou, L.; Lagaron, J. M. *J. Agric. Food Chem.* **2010**, *58*, 6884.
26. Sanchez, M. D.; Hilliou, L.; Lagaron, J. M. *J. Agric. Food Chem.* **2010**, *58*, 12847.
27. Van de Velde, F.; Pereira, L.; Rollema, H. S. *Carbohydr. Res.* **2004**, *339*, 2309.
28. Moreira, R.; Chenlo, F.; Torres, M. D.; Silva, C.; Prieto, D. M.; Sousa, A. M. M.; Hilliou, L.; Gonçalves, M. P. *Drying Technol.* **2011**, *29*, 1058.
29. Singh, P. C.; Singh, R. K. *J. Food Process. Preserv.* **1996**, *20*, 203.
30. Larotonda, F. D. S. PhD thesis, University of Porto, **2008**.
31. Gabriele, D.; de Cindio, B.; D'Antona, P. *Rheol. Acta.* **2001**, *40*, 127.
32. Torres, M. D.; Fradinho, P.; Raymundo, A.; Sousa, I. *Food Bioprocess Technol.* **2014**, *7*, 1171.
33. Ahmad, F. B.; Williams, P. A. *J. Agric. Food Chem.* **2001**, *49*, 1578.
34. van Soest, J. J. G.; Vliegthart, J. F. G. *Trends Biotechnol.* **1997**, *15*, 208.
35. Jenkins, P. J.; Donald, A. M. *Carbohydr. Res.* **1998**, *308*, 133.
36. Han, J. H.; Floros, J. D. *J. Plast. Film Sheet.* **1997**, *13*, 287.
37. Karbowiak, T.; Hervet, H.; Léger, L.; Champion, D.; Debeaufort, F.; Voilley, A. *Biomacromolecules* **2006**, *7*, 2011.
38. Abd El-Kader, M. F. H.; Ragab, H. S. *Ionics* **2013**, *19*, 361.
39. Khutorsky, V. E.; Lang, S. B. *J. Appl. Phys.* **1997**, *82*, 1288.
40. Kohyama, K.; Kim, K. Y.; Shibuya, N.; Nishinari, K.; Tsutsumi, A. *Carbohydr. Polym.* **1992**, *17*, 59.
41. Briones, A. V.; Ambal, W. O.; Estrella, R. R.; Pangilinan, R.; De Vera, C. J.; Pacis, R. L.; Rodriguez, N.; Villanueva, M. A. *Mar. Biotechnol.* **2004**, *6*, 148.
42. Beck, M. I.; Tomka, I.; Waysek, E. *Int. J. Pharm.* **1996**, *141*, 137.
43. Baldwin, E. A.; Nisperos-carriedo, M. O.; Hagenmaier, R. D.; Baker, R. A. *Food Technol.* **1997**, *51*, 56.
44. Debeaufort, F.; Voilley, A. *J. Agric. Food Chem.* **1997**, *45*, 685.
45. Allen, L.; McGill, J. N.; Nelson, A. I.; Steinberg, M. P. *Food Technol.* **1963**, *17*, 1437.
46. Ashley, R. J. In *Polymer Permeability*; Comyn, J., Ed.; Elsevier: London, **1985**; p 269.
47. Garcia, M. A.; Pinotti, A.; Zariwsky, N. E. *Starch/Stärke* **2006**, *58*, 453.
48. Anker, M.; Berntsen, J.; Hermansson, A. M.; Stading, M. *Innov. Food Sci. Emerg. Technol.* **2002**, *3*, 81.
49. McHugh, T. H.; Krochta, J. M. *J. Agric. Food Chem.* **1994**, *42*, 841.
50. Smith, S. A. In *Wiley Encyclopedia of Packaging Technology*; Bakker, M., Ed.; John Wiley & Sons: New York, **1986**, p 514.
51. Salame, M. Barrier polymers. In *the Wiley Encyclopedia of Packaging Technology*; Bakker, M., Ed.; John Wiley & Sons: New York, **1986**, p 48.
52. Shellhammer, T. H.; Krochta, J. M. *J. Food Sci.* **1997**, *62*, 390.
53. Taylor, C. C. Cellophane. In *Wiley Encyclopedia of Packaging Technology*; Bakker, M., Ed.; John Wiley & Sons: New York, **1986**, p 159.