



Polyvinyl alcohol-based films plasticized with an edible sweetened gel enriched with antioxidant carminic acid

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ABSTRACT

Edible sweetened gels are commonly used in bakery products. The aim of this work is to show that certain edible gels can be used as functional modifiers for biodegradable polymers. These gels are rich in glucose and sugars, containing much less water. To date, sugars (glucose, maltose, sucrose, and D-allulose), have also been used as natural plasticizers for polysaccharides to form edible films. In this work, we prepared an edible gel based on glucose, sugar and carrageenan as a gelling agent and tested the gel's plasticizing effect on polyvinyl alcohol, PVA. Carminic acid, a natural pigment and a powerful antioxidant with antiradical activity, was added to the gels. The optimum plasticizing effect was obtained from 1:1 gel: polymer mixing ratio with 28.6 wt% total sugars. Carminic acid also assisted with low oxygen permeation (OP, 3.4 cm³ µm².day.atm) values due to its oxidative radical scavenging chemistry. In aqueous and ethanoic solutions, the films released carminic acid in a sustained manner and within 36 h, strong inhibition was measured against standard stable free-radical molecules known as DPPH and ABTS⁺. Finally, the films demonstrated effective color change upon exposure to ammonia vapors that can be exploited towards food spoilage detection. These materials could be effectively used as freestanding, protective antioxidant barrier films or can be laminated with other hydrophobic thermoplastics for general packaging applications.

1. Introduction

Increasing environmental concerns as well as excessive plastic pollution in our seas and oceans have fueled the development of alternative biodegradable films and coatings from various types of biopolymers (Contardi et al., 2020; Suaria et al., 2016; Wang et al., 2021). A significant portion of biopolymers, particularly originating from polysaccharides is not in the form of thermoplastics unless they are chemically modified such as acetylation or grafting (López et al., 2015; Matet et al., 2013; Simon et al., 1998). Moreover, films produced from many of these polysaccharides or hydrocolloids are very brittle with poor elongation and excessive water uptake properties (Aravamudhan et al., 2014; Bayer, 2021a,b; Ross-murphy et al., 1998; Wollerdorfer and Bader, 1998). Edible films also suffer from these problems (Otoni et al., 2017). Hence, extensive research efforts have been devoted to improving the quality and application of biodegradable and edible films and coatings with better mechanical, barrier and sensorial characteristics, while preserving their biochemical, physicochemical and microbiological stability.

Plasticizers are key additives to address some of the afore mentioned issues (Vieira et al., 2011). Many biodegradable films obtained from hydrocolloids are plasticized with sugars (glucose, galactose, sucrose) and polyols (glycerol and sorbitol) (Piermaria et al., 2011; Jouki et al., 2013, 2021, 2021; Jouki et al., 2013a,b; Jouki et al., 2021a,b). In many cases, the addition of sugar or monosaccharide based plasticizers have improved their water vapor permeability and mechanical properties without any phase separation issues (Bocqué et al., 2016). Sugars were also effectively used to modify the mechanical properties of edible starch films (Ployetchara and Gohtani, 2018). For instance, the work of Veiga-Santos et al. (2007) showed that adding sucrose or inverted sugar (also known as invert sugar, an edible mixture of glucose and fructose), in cassava starch films resulted in increased elongation at break values. Zdanowicz et al. (2019) reported the use of sugars and glycerol mixtures as novel plasticizers for potato starch to form low transition temperature mixtures, exhibiting good plasticizing activity leading to homogenous transparent, flexible thermoplastic starch (TPS) materials. Very recently, deep eutectic solvents based on blends of sugars, urea and polyols produced very effective solvents as well as plasticizers for potato starch

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films (Zdanowicz, 2021). Similarly, corn or glucose syrup or high fructose corn syrup has been used as plasticizers for alginate based nano-cellulose composite films (Azeredo et al., 2012). Moreover, sugar-bound pectin obtained from fruit and vegetable wastes were found to act as effective plasticizers for alginate films, as well (Di Donato et al., 2020).

Review of the literature indicates that sugar or monosaccharide based plasticizers have been extensively used for starch, alginate, zein and pectin films (Kalichevsky et al., 1993) and were rarely implemented in other biodegradable polymers such as polyvinyl alcohol (PVA) except for plasticizers in starch/PVA blends (Parvin et al., 2011). Yazdani et al. (2020) used sugar alcohol plasticizers in PVA to produce latent heat-storing bio-based polymers. Although synthetic in nature, PVA possesses many useful properties, such as excellent chemical resistance, good film forming capability (Aslam et al., 2018), good emulsion stability and adhesion strength, water solubility, high thermal stability (Russo et al., 2009), and excellent biocompatibility and biodegradation (Marušincová et al., 2013). PVA has been successfully implemented in food technology research in many different forms, such as antibacterial and antioxidant films (Silva et al., 2021), protective gels (Taherian et al., 2019), bilayer and laminates (Song et al., 2020) and as nanocomposites (G. Liu et al., 2014).

Confectionery gels are composed of high sugar components of sucrose and glucose syrup, along with gelling components such as gelatin, carrageenan or pectin, and food acids such as citric, lactic and acetic acids and colorants (Burey et al., 2009). Glucose syrups are principally shelf-stable and contain no preservatives to prevent microbial growth. This is because high solids content with reduced water activity are much below the microbial growth condition levels (Burey et al., 2009; Taibi et al., 2021). Al-Ruqaie et al. (1997) studied the effect of sucrose/glucose syrup blend additions into pectin and gelatin biopolymers and measured transformation of protein or polysaccharides into rubbery states depending on the concentration of the added syrups. It has been also demonstrated that the type of the syrup such as glucose or corn syrup determined with varying “dextrose equivalent” or DE grading can significantly affect the gel properties and the release of flavoring agents from edible polymer films or pastilles (Lubbers and Guichard, 2003). Carrageenan, an algae-derived polysaccharide originating from Rhodophyta seaweed, is a highly preferred hydrocolloid in the formulation of edible gels. Carrageenan is a negatively-charged polyelectrolyte consisting of a sulfated polysaccharide chain, and as such, its structure is sensitive to ionic conditions including media pH and cation concentrations (Fenton et al., 2021; Rochas and Rinaudo, 1984). In warm aqueous media, gelling of carrageenan can be achieved with concentrations ranging from 0.6 wt% to 3 wt% concerning water (Fenton et al., 2021; Wen et al., 2021). Besides ions and pH levels, gelation dynamics and consistency of carrageenan are affected by sugar/syrups as co-solvents that have a direct impact on the gelation temperature and physical arrangement of the gel networks (Geonzon et al., 2020; Y. Liu et al., 2020). The earliest edible gels based on carrageenan developed for bakery products were prepared with 0.015–0.07 carrageenan/sugar (g/g) ratio (Arthur L. Moirano, 1981) and many commercial edible gels based on carrageenan are in use today.

In this work, we demonstrate that certain edible functional gels (i.e., antioxidant gels) can be used as effective plasticizers for biodegradable polymers. Unlike liquid formulations, food gels contain much less water while achieving the desired effect when added into various systems like emulsions, creams and polymer solutions. To this end, we prepared edible gels based on glucose syrup (~20%), sugar (~20%), and carrageenan (~0.85%) with acidity regulators such as citric acid, acetic acid; lactic acid and sodium lactate (all together <0.5%) along with food preservative potassium sorbate (<0.05%). The gels were colored with a natural food colorant known as carminic acid (~0.3%) (Frandsen et al., 2018; Q. Liu et al., 2021; Masár et al., 2020; Ordoudi et al., 2018). Carminic acid (a natural red pigment produced by *Dactylopius coccus* C. insects) is also known to be a very potent natural antioxidant (González

et al., 2010). Many antioxidant-modified polymer films can potentially have much better food preservation properties compared to non-modified ones even if they possess good gas barrier properties. In addition, synthetic antioxidants such as butylated hydroxyl toluene (BHT) have limited use due to certain U.S. Food and Drug Administration (FDA) regulations. As such, carminic acid can be a possible alternative since its antioxidant properties are being recognized in medicine as well (Li et al., 2021). Viscoelastic properties of the gels were studied and the gels were dispersed in 10 wt% aqueous PVA solutions and the mixtures were cast as films. Thermomechanical properties of the gel modified PVA films were studied as a function of gel concentration as well as their water uptake, and oxygen gas transmission properties. Gel modified PVA films were effectively plasticized and demonstrated impressive oxygen barrier properties and good radical scavenging activity. Finally, the gel-modified films were laminated with polycaprolactone (PCL) films in order to improve their hydrophobicity without compromising the oxygen barrier properties.

2. Materials and methods

2.1. Materials

Food grade refined κ -carrageenan was supplied by F Gutkind & Co Ltd, England. According to the supplier 1 wt% solution in water at 20 °C has a pH level 8–11 with 12% moisture loss upon drying and particle size below 250 μ m. Glucose syrup (3883) was donated by Roquette Italia S.P.A. According to manufacturer specifications, it is an aqueous solution containing a mixture of glucose, oligosaccharides and polysaccharides obtained by hydrolysis of starch with a dextrose equivalent of DE 36–39 wt% and containing 21 wt% water. Carminic acid, citric acid (ACS reagent grade), DL-lactic acid (90%), acetic acid (ACS reagent grade), sodium DL-lactate (ReagentPlus), potassium sorbate (purum p.a., $\geq 99.0\%$) were all purchased from Sigma-Aldrich, Italy and used as received. Sugar granules were purchased from a local supermarket. Poly (vinyl alcohol), PVA, Mw 89,000–98,000, 99+% hydrolyzed, Polycaprolactone (PCL) pellets with average Mn 80,000 and 30% aqueous ammonium hydroxide (NH₄OH) solution were purchased from Sigma-Aldrich, Italy. Deionized water was obtained from a Milli-Q Advantage A10 Ultrapure Water Purification system (Merck, Darmstadt, Germany). DPPH (2,2-diphenyl-1-picrylhydrazyl) and ABTS⁺ (2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) were purchased from Alfa Aesar (Kandel, Germany) and ethanol ($\leq 100\%$) was purchased from Merck and used as received.

2.2. Gel preparation

The gel preparation was based on the classical bakery gel descriptions (Arthur L. Moirano, 1981; Lagarrigue et al., 2014; Towle,

Table 1

Edible gel components. The gel constituents are typical for colored bakery gels that contain additives such as acidity regulators, sugar crystallization inhibitors and anti-mold additives. Control samples made only for antioxidant testing excluded additives marked with (*) in the table. Water percent also includes water in glucose syrup.

Ingredient	Percent (wt.%)	Function
Water	58.4	Solvent
Glucose syrup	20.0	Sweetness
Sugar	20.0	Sweetness
Carrageenan	0.85	Gelling
Citric acid (*)	0.10	Crystallization inhibition
Acetic acid (*)	0.10	Crystallization inhibition
Lactic acid (*)	0.10	Crystallization inhibition
Sodium lactate (*)	0.10	Acidity regulator
Potassium sorbate (*)	0.05	Mold inhibitor
Carminic acid	0.30	Colorant/antioxidant

1976). In these works, κ -carrageenan was used as the gelling agent. Table 1 shows the ingredients of the gel and their relative percentage and function. Glucose syrup, sugar, citric, acetic and lactic acids along with sodium lactate and potassium sorbate were dispersed in hot water at 80 °C under constant stirring upon dispersion of all the ingredients, κ -carrageenan powder was slowly added to the system and allowed to dissolve under constant stirring. After dissolution of κ -carrageenan, the solution was cooled to 40 °C slowly and at this point carminic acid was added transforming the viscous solution into a dark red color (see Fig. 1a). Carminic acid was not added at the initial hot stage in order to ensure its antioxidant properties were not altered at high temperatures.

2.3. Preparation of the polymer films

A 10 wt% PVA polymer solution in water was prepared by dissolving PVA powder in hot water under constant stirring at 90 °C. Once the polymer was completely dissolved, it was slowly cooled down to room temperature. The polymer films were prepared by combining 1 g of gel with 10 g of the polymer solution in order to produce dry films with 1:1 (gel: polymer) ratio. Once the gel was completely dispersed in the solution, the blend was poured into square plastic petri dishes and allowed to dry under ambient conditions for 48 h as shown in Fig. 1b. The films could be easily peeled off and remained self-standing and soft (see Fig. 1c–d).

As a result, a dry film typically contains 14.3 wt% glucose, 14.3 wt% sugar, 0.6 wt% carrageenan, 0.21 wt% carminic acid and 70.6 wt% PVA. In other words, the total monosaccharide based plasticizer content in the films is 28.6 wt%. Average film thickness was around 80–90 μm . For the antioxidant characterization experiments of the films, control films without the additives (indicated by (*) in Table 1) were also made in order to ensure the antioxidant effect of carminic acid was properly identified.

2.4. Rheological characterization of the gel

Rheological characteristics of the gels were made on a rotational modular rheometer Anton Paar MCR 102 (Anton Paar GmbH, Graz,

Austria). It is equipped with a stainless steel cone-and-plate geometry with a cone angle of 1° and 60 mm in diameter (gap size = 210 μm). The bottom plate was heated to 80 °C before measurements. The gels were placed over the bottom plate and allowed to relax for about 10 min at 80 °C to ensure the viscous liquid state is maintained. Silicone oil was placed around the perimeter of the sample to prevent water evaporation during measurements. Strain sweep measurement range was maintained between 0.1 and 10,000% with 1 rad/s angular frequency.

Each test was repeated in triplicate. To study viscoelasticity as a function of temperature, a temperature sweep from 80 °C to 20 °C was applied holding the system at 20 °C for 5 min, and then heating up to the final temperature, 80 °C. The gelation and melting temperature was defined as the temperature where elastic and plastic moduli were equal, $G' = G''$. The cooling and heating rates were 1 °C/min under a fixed strain of 1% and angular frequency of 100 rad/s. These measurements were used to assess the linear viscoelastic properties of the samples. Thixotropy tests were performed at 23 °C by shearing the gel from zero shear to 100 s^{-1} (in 1 min), holding there for 2 min (at 100 s^{-1}), then ramping down to zero shear again in 1 min. This constituted one hysteresis loop. After a 10 min fluid rest period, the shearing experiment was then repeated forming the second hysteresis loop. Note that thixotropy is a decrease in the apparent viscosity under shearing, followed by a gradual recovery when the shear is removed. The effect is time dependent. If the viscosity reduces and immediately returns after shearing, the material is not thixotropic (no hysteresis loop appears) but just 'shear thinning'.

2.5. Thermal compression into multiple film structures

Polycaprolactone (PCL) pellets (1 g) were placed between two non-stick plastic films (PTFE, Teflon) and pressed into a film form using a hydraulic hot press at 80 °C under 570 kgf for 20 s. After removal from the press and cooling to room temperature, a PCL film of about 65 μm thickness and 8 cm in diameter was formed. Another film was also produced using the same process above. In the meantime, a PVA film plasticized with 28.6 wt% carminic acid gel was kept in an oven at 50 °C for ½ hour to ensure adsorbed water is removed. After this, the film

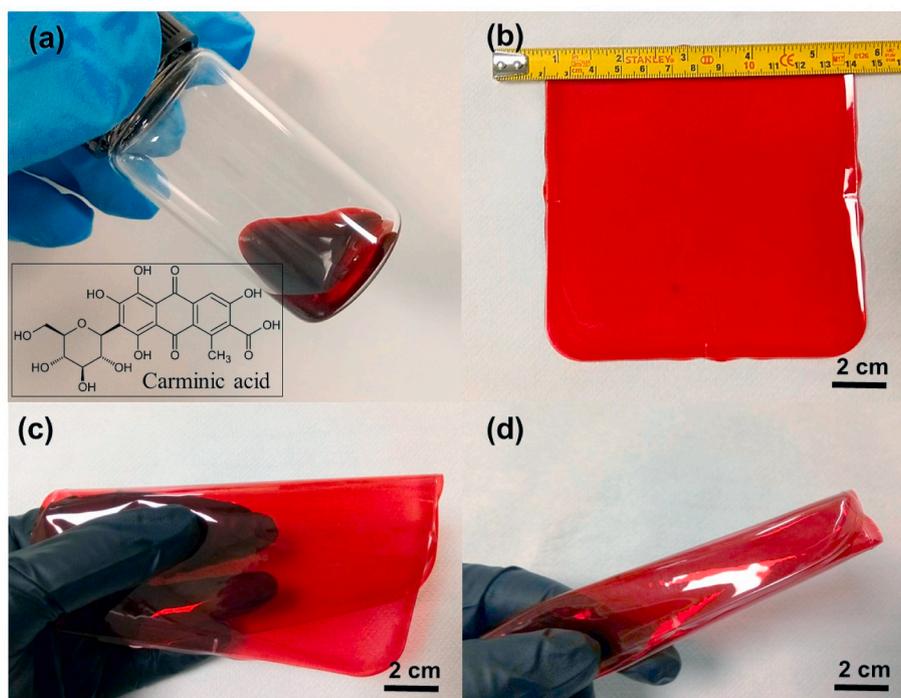


Fig. 1. Photographs of (a) carrageenan-based gel containing carminic acid, (b) PVA-gel film after drying and removal from the plastic mold, (c) and (d) photographs showing gel plasticized films that are easily foldable and soft.

(rectangular, 5 × 4 cm) was sandwiched between the two PCL films and the multilayer system was covered with the non-stick plastic films. The sandwich was compressed with the hydraulic press under the same conditions indicated above for 20 more seconds and the final PCL-PVA-PCL multilayer film with a thickness of 115 µm was produced.

2.6. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements

Dry film cross section images were acquired by a scanning electron microscope (SEM, JEOL JSM-6490AL) with 10 and 15 kV accelerating voltage. Specimens were coated by a thin (15 nm) gold layer. The surface morphology of the dried gel and the films were scanned with atomic force microscopy (AFM) under ambient conditions using a Park System AFM instrument (XE-100) in true non-contact mode. An anti-vibration table (Table Stable TS-150) with an acoustic enclosure was used to isolate the equipment from external disturbances. Single-beam silicon cantilevers tips (PPP-NCHR-10) were used for scanning the surfaces with 10 nm nominal radius and 42 N/m elastic force constant. The resonance frequency was set at 280 kHz. The scan rate was between 0.2 and 1.0 Hz.

2.7. Thermal analysis and attenuated total reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy

Differential scanning calorimetry (DSC) measurements were made with a DSC Q20 (TA Instruments, New Castle, DE, USA) from 0 °C to 300 °C with dry nitrogen flow at 50 mL/min at 10 °C/min. Dry gel and plastic film samples (~4 mg) were cut and conditioned at 55% relative humidity (RH) in a glove box for 3 days. Afterwards, samples were hermetically sealed in aluminum pans inside the glove box and a pinhole was punctured just before placing them in the instrument. The thermal degradation characteristics of the dry gel and the plastic films were measured by a standard thermo-gravimetric (TGA) instrument, i.e., TGA Q500 by TA Instruments (New Castle, DE, USA). Measurements were taken from 3 to 5 mg samples placed on aluminum pan sample holders under nitrogen atmosphere with a flow rate of 50 mL/min (range: 20 °C–800 °C) with a heating rate of 10 °C/min. FTIR scans were made with a single-reflection attenuated total reflection (ATR) accessory (MIRacle ATR, PIKE Technologies, Madison, MI, USA) coupled to a Fourier Transform Infrared (FTIR) spectrometer (Vertex 70V, Bruker, Ettlingen, Germany). All spectra were recorded within the 3800 to 600 cm⁻¹ wavenumber range with a resolution of 4 cm⁻¹, gathering 128 scans to reduce the spectral noise. The built-in OPUS software was used to analyze the data.

2.8. Mechanical characterization and X-ray diffraction (XRD) measurements

Stress-strain behavior of the films were measured by uniaxial tensile tests using a dual column Instron 3365 universal testing machine (High Wycombe, England). Dog-bone shaped samples were punched with a gauge length of 25 mm and a width of 4 mm. Samples were strained with a rate of 10 mm/min. Stress-strain curves were measured at 25 °C and 44% relative humidity (RH). A minimum of ten measurements were taken from each film and average results were reported. Tensile strength was calculated from the slope of the linear part of stress-strain curve before the elastic limit. Both Young's (elastic) modulus and elongation at break values were determined using the built-in software of the tensile tester.

Film crystallinity was measured using a Rigaku SmartLab X-ray diffractometer, equipped with a 9 kW CuK α rotating anode and operating at 40 kV and 150 mA. A Göbel mirror was installed to form a parallel beam suppressing the Cu K β radiation (1.392 Å). The diffraction patterns were collected at room temperature over an angular range 8°–50°, with a step size of 0.05°. High Score 4.1 software from PANalytical was used for phase identification. For XRD peak identification, we have

used the Joint Committee on Powder Diffraction Standards (JCPDS) card No. 83–0520.

2.9. Antioxidant activity measurements (DPPH, ABTS)

Two different antioxidant assays, namely, ABTS^{•+} (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) and DPPH[•] (2,2-diphenyl-1-picrylhydrazyl) were used. Solutions (ethanol for DPPH[•] and water for ABTS^{•+}) of both radicals were prepared according to our previous work (Quilez-Molina et al., 2020a,b). About 80 mm² round shaped films were immersed into 3 mL of radical solution. Upon release of carminic acid from the films into the solution, changes in the UV absorption of the radicals took place compared to the control solutions. The more antioxidant was released in time, the more the intensity of the peaks increased. This was monitored for 72 h using Cary JEOL UV-spectrophotometer. The characteristic absorption peaks of ABTS^{•+} and DPPH are at 734 nm and 517 nm, respectively. All measurements were performed at least five times to ensure reproducibility.

2.9.1. Water uptake and oxygen permeability

Before water uptake measurements, films were dried in a desiccator to eliminate any adsorbed moisture in the films. This was monitored as changes in the weight of the films during the conditioning process with a sensitive electronic balance. Dried films were placed in a sealed chamber under different humidity conditions (RH) at 25 °C, namely 0%, 15%, 45%, 85% and 100%. Once the equilibrium was reached (in general after 48 h), each sample was weighed again and the amount of water uptake was calculated as the difference. Measurements were made in triplicate. The oxygen permeation characteristics of pure PVA and PVA-gel films were measured using an Oxysense 525oi device (Oxysense, USA) equipped with a film permeation chamber, following ASTM Method F3136-15 standard. The tests were conducted under 24 °C and 40% relative humidity. Briefly, the permeation chamber is a cylinder divided in sections (sensing well and driving well). The films were cut into rectangular pieces in 6 cm × 6 cm size and inserted between the two wells. The sensing well is equipped with a fluorescence sensor known as oxydots that measures oxygen concentration directly. This section was purged with nitrogen while the driving well was open to ambient air. An OxySense fiber optic system measures the oxygen concentration from the oxydots, at specific time intervals. These readings were converted to oxygen transmission rate (OTR) using the Oxysense OTR built in software. A minimum of 10 measurements were collected from each film with R² = 0.95.

Gas permeation, moisture uptake and mechanical properties data were initially assessed by analysis of variance (ANOVA), afterwards, a Duncan's multiple range test was used to identify significant (p < 0.05) differences among the samples tested.

2.9.2. Response of the PVA-gel film against ammonia vapors

Since carminic acid color changes toward magenta-red at pH levels above 10, the PVA-gel film (thickness: 90–100 µm, diameter: 14 mm) was exposed to ammonia (NH₃) vapors generated in a closed petri dish with dimensions 100 mm in diameter and 20 mm in height by enclosing 500 µl NH₄OH solution. The color changes of the film were recorded up to 15 min and further analyzed with UV-visible spectroscopy to investigate their potential as pH indicators.

CIELab color space is a tool that mimic the human eye color perception (Zia et al., 2021) and used as a scientific proof to the color changes in a similar way as perceived by the human eye. The three color parameters of the CIELab color space are lightness of the color (L) and its hue (a and b) were collected from the images taken from a reflex camera (Canon EOS 5D Mark II) under same light and distance by using free mobile application "deltacolor". The total color difference (ΔE) calculated from the following Equation (Zia et al., 2021).

$$\Delta E = \sqrt{[(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]} \quad (1)$$

When the value of ΔE is greater than 3.5, the color difference is clearly perceivable by experienced and unexperienced observers (Zia et al., 2021).

2.9.3. Antioxidant activity of the PCL laminated films

The antioxidant activity of the PCL laminated films was carried out using the method of Blois (1958) with modifications (Palazzo et al., 2020). Different weights of laminated film samples were added to 1 mL of acetone solutions and the solutions were added to 3 mL of an ethanolic solution of DPPH (1×10^{-4} M). The samples were agitated and placed in the dark for 30 min at room temperature. Then, the absorbance was measured at 517 nm. As a negative control, an ethanolic solution of DPPH (1×10^{-4} M) was used in which 100% pure acetone was added. The antioxidant activity was calculated on the basis of the decrease in absorbance due to reaction with the radical molecule. Spectroscopic procedures similar to Sec. 2.9 were followed. All determinations were performed in triplicates.

3. Results and discussion

3.1. Rheological properties

κ -carrageenan is a natural sulfated polysaccharide extracted from red seaweed mainly belonging to Chondrus, Gigartina, and various Eucheuma species (Yang et al., 2018). It is a very common food additive that functions as thickener, stabilizer, and texturing agent also for cosmetic and pharmaceutical products (Yang et al., 2018). κ -carrageenan forms a thermo-reversible gel in aqueous solution. In food science and technology, stability, viscoelastic and rheological properties of carrageenan-based gels are carefully studied, as these properties are very important to maintain food quality, sensory characteristics and shelf life (Huang et al., 2021; Míšková et al., 2021). Maintenance of linear viscoelastic behavior in edible gels is important for their processing into composites and even for 3D printing (Rahman et al., 2020). We conducted dynamic strain sweep analysis on the gel sample to ensure that the linear viscoelastic region (LVR) remains stable and reversible at 1% strain rate, even beyond and the gel structure was not altered as shown in Figure S1 (Supplementary Information). Further rheological and thixotropic properties of the gel shown in Fig. 1a are plotted in Fig. 2. Note that carminic acid did not affect the rheological properties of the gel. Fig. 2a and b shows the viscoelastic modulus variations with temperature during heating (80 °C) and cooling cycles (20 °C) for two gel systems; one without glucose + sugar and one with, respectively. During cooling, between 80 °C - 40 °C, both elastic (G') and viscous

modulus (G'') increased slightly with cooling due to loss of molecular chain mobility; and the G'' remained above G' , suggesting that the gel was in solution state. Further cooling from this point on (40 °C) resulted in dramatic increases in both G' and G'' and G' increased much faster than G'' . When G' and G'' crossover, the point is known as the gelation point (or temperature), in other words, gelling point is the critical temperature at which $G' = G''$. At temperatures lower than the gelation point, both G' and G'' continuously increased, and G' became higher than G'' , indicating transformation from solution state to gel state due to helix aggregation (Ploypetchara and Gohtani, 2018). During the heating cycle, the gel network is disrupted that is reflected as reductions in both G' and G'' . Further increase in temperature, however, caused gel-to-solution transition at which G' and G'' crossed over again but at a higher temperature. The temperature at which this occurs is defined as gel or melting point. At higher temperatures beyond the melting point, the value of G'' remained greater than G' , indicating that the gel network transformed into a viscous liquid solution, probably induced by the dissociation of helical aggregates and broken gel network (Ikeda et al., 2001).

In the case of films made with glucose and sugar plasticizers as shown in Fig. 2b, differences were observed during both cycles. Both G' and G'' decreased significantly after 55 °C that is a higher temperature compared to the behavior observed in Fig. 2a. During cooling, gelling point at $G' = G''$ occurs at a higher temperature near 55 °C that is much higher than 40 °C in Fig. 2a. As such, the gel-like state is more stable at higher temperatures in the presence of the plasticizers. This could be attributed to the fact that sugar molecules can interact with polysaccharides limiting their chain mobility under strain (Ploypetchara and Gohtani, 2018). This is generally reflected as changes in viscoelastic behavior and crystallinity of the polysaccharide polymer chains. For instance, flow behavior index (the degree of non-Newtonian characteristics of the fluid) were reported to increase when plasticizer sugars were added to starch (Yoo and Yoo, 2005). The same argument holds for the transformation to a fluid-like state during heating at which a much higher temperature was measured at 65 °C instead of 55 °C in Fig. 2a.

Thixotropic properties of the gels were evaluated by rheological measurements as shown Fig. 2c. In general, the thixotropic property can be measured by a shear stress–shear rate dependent rheological analysis known as flow curve in which appearance of a hysteresis loop is investigated. Fig. 2c shows the typical flow curves of the gels with and without glucose + sugar plasticizers. For both gels, thixotropic behavior was observed during 1st and 2nd scans. A crucial distinction for thixotropic behavior compared to plastic flow is the fact that the reversibility of the stress-strain rate does not occur. Thus, in Fig. 2c, on steadily increasing the shear rate the viscosity (the tangent or the slope) fell steadily, but on reversing the direction of change of shear strain rate, the

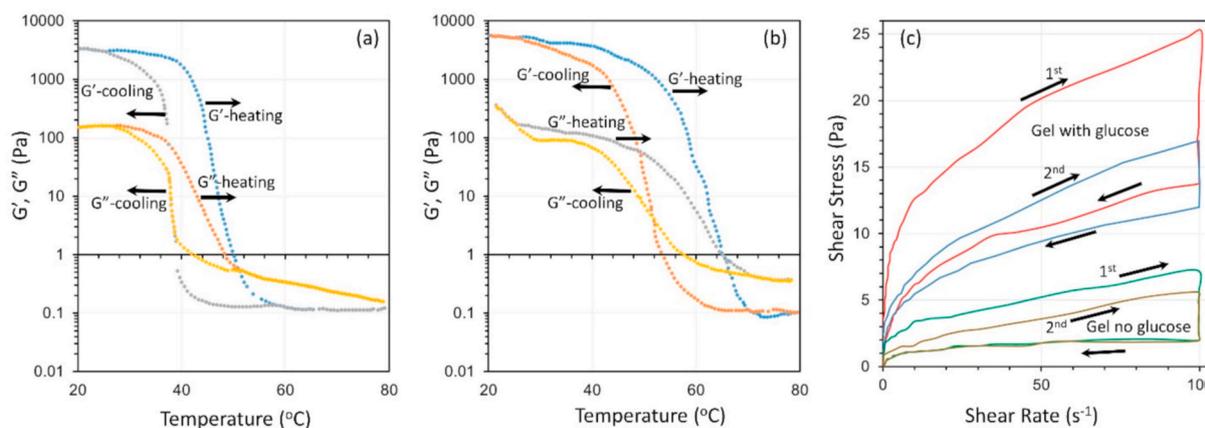


Fig. 2. Changes in elastic and viscous moduli as a function of temperature in gel (a) and a gel without glucose + sugar (b) and (c) Thixotropic (rheopectic) scans for both gels with hysteresis behavior. Loops were obtained by reversing the shear rate.

original curve was not traced. In the case of gels containing glucose and sugars, the viscosity changes occurred at higher values including the second cycle even though the viscosity was further declined upon second cycle trace. In the case of gels with no glucose and sugar, a similar trend is seen but the second trace is closer to the first trace compared to the gels with plasticizers. This may be due to the fact that in the presence of the plasticizers, the first trace would not sufficiently provide shear energy to break sugar molecule-polysaccharide interactions but in the second trace, more energy overcomes these interactions and the viscosity was further reduced and hysteresis loop was smaller (Ghica et al., 2016).

3.2. Micromorphology of the films

Fig. 3 shows both AFM surface morphology and the SEM cross-section images of pure PVA and glucose and sugar plasticized PVA-gel films. In Fig. 3a, the AFM topography of the dry gel film is shown which was spread evenly over a silicon wafer. From the image of Fig. 3a, upon drying, no sugar re-crystallization was observed indicating that effective mutarotations (conformational sugar molecular changes in solution) took place in the gel due to added weak acids as shown in Table 1 (Hartel et al., 2009). Particularly lactic and citric acids are very effective in forcing sugar molecules to undergo mutarotations (Hartel et al., 2009). The film surface roughness was approximately 7.0 nm. The AFM images of the gel film without the crystallization inhibitors listed in Table 1 are shown in Figure S2 (Supplementary Material). Therein, rougher surface roughness features appeared to have formed. In Fig. 3b, the surface microscale morphology of pure PVA film is shown. The morphology indicates several valleys (differentiated by light and dark areas) leading to a surface average roughness of about 23.0 nm. The morphology of the gel-polymer composite with glucose and sugars (Fig. 3c) showed a somewhat smoother surface average roughness that was measured to be around 13.5 nm. Similarly, the SEM cross-section images (Fig. 3d and e) showed that modification of PVA with the gel does not cause any phase separation or crystallization of any mono or polysaccharides and the system was found to be highly homogenous. Changes in roughness due to the gel modification of the PVA matrix can

be attributed to dispersion of sugars in the matrix. If the sugars are not dispersed well, they can cause an increase in the roughness of the films. However, as long as these changes or increase in roughness values are kept within the same order of magnitude, no major deviations in film properties should be expected.

3.3. Spectroscopic and thermal properties of the films

FTIR, TGA and DSC measurements of some of the raw materials i.e., carrageenan, PVA, glucose and sugar, the gel and the PVA-gel films are shown in Fig. 4. Specifically, Fig. 4a shows the FTIR profiles of pure carrageenan and the gel upon drying. The major wavenumbers characteristic to both spectra were identified on the plots. Typical OH stretching band at 3400 cm^{-1} is very typical for poly- and mono-saccharides polymeric units with covalently bonded OH. Aliphatic CH and CH_2 stretching bands are recorded at 2920 cm^{-1} . The small band at 2350 cm^{-1} is ascribed to C=C conjugated bonds. The band at 1244 cm^{-1} can be attributed to C-O stretching and the bands at 1058 cm^{-1} , 914 cm^{-1} , 840 cm^{-1} and 690 cm^{-1} can be ascribed to CO-O-CO stretching, S=O stretching, S-O bonds and C-S bonds due to carrageenan, respectively (Cui et al., 2016; Pereira et al., 2003). Similarly, Fig. 4b demonstrates FTIR spectra of pure PVA and PVA-gel films with characteristic bonding wavenumbers identified. The band at 3335 cm^{-1} is the OH stretching band due to alcohol chemistry and the bands at 2911 cm^{-1} and 2847 cm^{-1} are allocated to alkane C-H stretching and aldehyde (vinyl) CH stretching bonds, respectively. The signal at 1700 cm^{-1} are ascribed to C=C and C=O bonds (due to partially hydrolyzed grade of PVA used (Sharma et al., 2009) and the bands between 1356 cm^{-1} - 1420 cm^{-1} can be attributed to C-H bending, C-O stretching and S=O stretching in the case of the films with the gel. The bands appearing at 1250 cm^{-1} and 1075 cm^{-1} are ascribed to C-O bending that might be due to alkoxy interactions. The band at 840 cm^{-1} can be attributed to C-H sp^2 bending but also to aromatic C-H bonds due to carminic acid, although its concentration may be too small to be detected by FTIR (Mecozzi and Sturchio, 2017). In summary, the FTIR spectra indicate that there are no new chemical structures and as such the gel and PVA form a physical blend with no permanent chemical bonding formation among

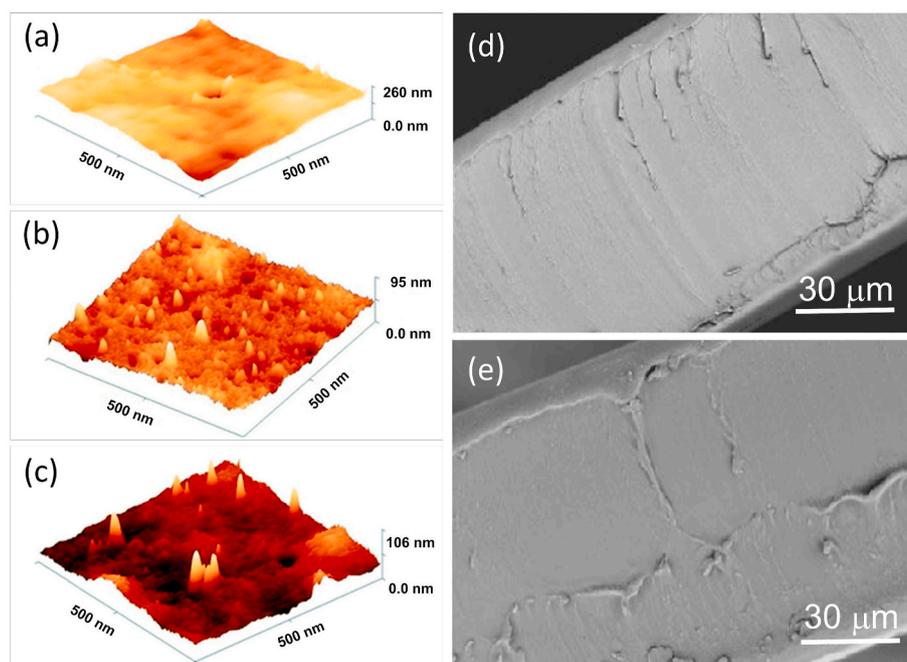


Fig. 3. (a) AFM surface topography of the gel dried on a smooth silicon wafer surface, (b) surface morphology of pure PVA film surface, (c) PVA-gel composite with glucose and sugar plasticizers, (d) SEM cross section of pure PVA film and (e) SEM cross section of the glucose and sugar plasticized PVA film. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

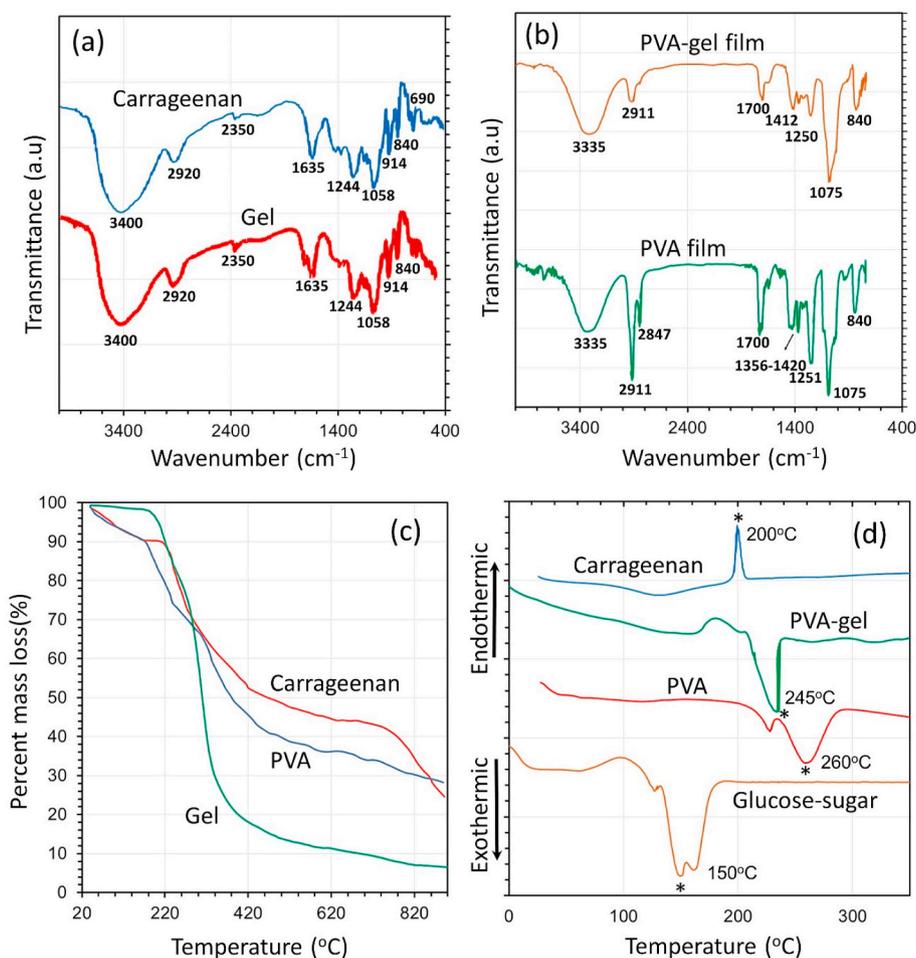


Fig. 4. (a) FTIR spectra of pure carrageenan and the edible gel, (b) FTIR spectra of pure PVA film and the PVA-gel composite, (c) TGA thermal degradation of pure carrageenan, pure PVA and the gel and (d) DSC profiles of pure carrageenan, pure PVA, glucose-sugar, and the PVA-gel composite films.

the polymer, the sugar molecules, the polysaccharide and the carminic acid.

Thermal degradation of the dried gel in Fig. 4c occurred more rapidly compared to pure carrageenan and PVA. This is attributed to the existence monosaccharide structure of the glucose and sugars that constitute the main ingredients of the dried gel. The full thermal degradation of all the materials started at about 220 °C but both carrageenan and PVA had a much slower rate of mass loss with higher residues remaining after 820 °C (approximately 30%) compared to the gel which produced less than 10% ash or residue. Similarly, the DSC properties of some selected films are shown in Fig. 4d.

Pure carrageenan demonstrated a slight exothermic recrystallization event and at 200 °C, a glass transition event with enthalpy relaxation was measured indicated by an abrupt and linear rise in the baseline signal and leveling out at around 125 °C. Pure PVA (partially hydrolyzed) demonstrated recrystallization point peaks between 220 °C and 250 °C. These two exothermic events can be correlated to amorphous phase changes that show a sudden change in specific heat capacity or shift in the baseline. This behavior resembles that of polymers with eutectic compounds/impurities that can be due to the partially hydrolyzed state of PVA (Belfiore and Ueda, 1992). The DSC profile of the PVA-gel film showed a broad endothermic event at around 180 °C that is characteristic of second order solid-solid transitions. These transitions occur as continuous change in the specific volume and entropy and include transitions associated with the emergence of orientation-induced order in polymeric chains or fluidic transformations that might be attributed to interactions between the monosaccharides and the PVA polymer chains (Cheng, 2008). The exothermic event at

220 °C is characteristic of re-crystallization point for semi-crystalline polymers such as PVA. Finally, for the glucose-sugar mixture, the endothermic peak at 150 °C is a typical behavior of rapid re-crystallization behavior of monosaccharides-based sweeteners such as sucrose (Beckett et al., 2006). The split of the peak in two could be related to the difference in the crystallization of sugar (sucrose) and glucose. The mixture also presented a broad endothermic event at around 100 °C that is also characteristic of second order solid-solid transitions, which occurred at a higher temperature in PVA-gel films. It can be concluded that the sugars definitely modify the endothermic and exothermic crystalline transformations (nucleation) in the PVA film. However, the PVA-gel film still shows a nucleation temperature of 245 °C implying that although reduced due to the presence of sugars, PVA still maintains its self-crystalline nature that allows retaining its other intrinsic properties such as very good oxygen gas barrier property.

3.4. Mechanical and crystallographic properties

Changes in the tensile strength (maximum stress value measured before break) and the elongation at break values of the PVA-gel films as a function of the added gel concentration are shown in Fig. 5a. Measurements were made at a low 5% RH in order to eliminate the effect of water or moisture on the film properties. Note that pure PVA had a tensile strength of about 22 MPa and elongation at a break value of about 40%. Modifying the films with 5 wt% and 10 wt% gel, reduced the tensile strength to 18 and 16 MPa, respectively and increased percent elongation before break values to 51% and 70%, respectively. Increasing the added gel concentration to 28.6 wt% did not significantly

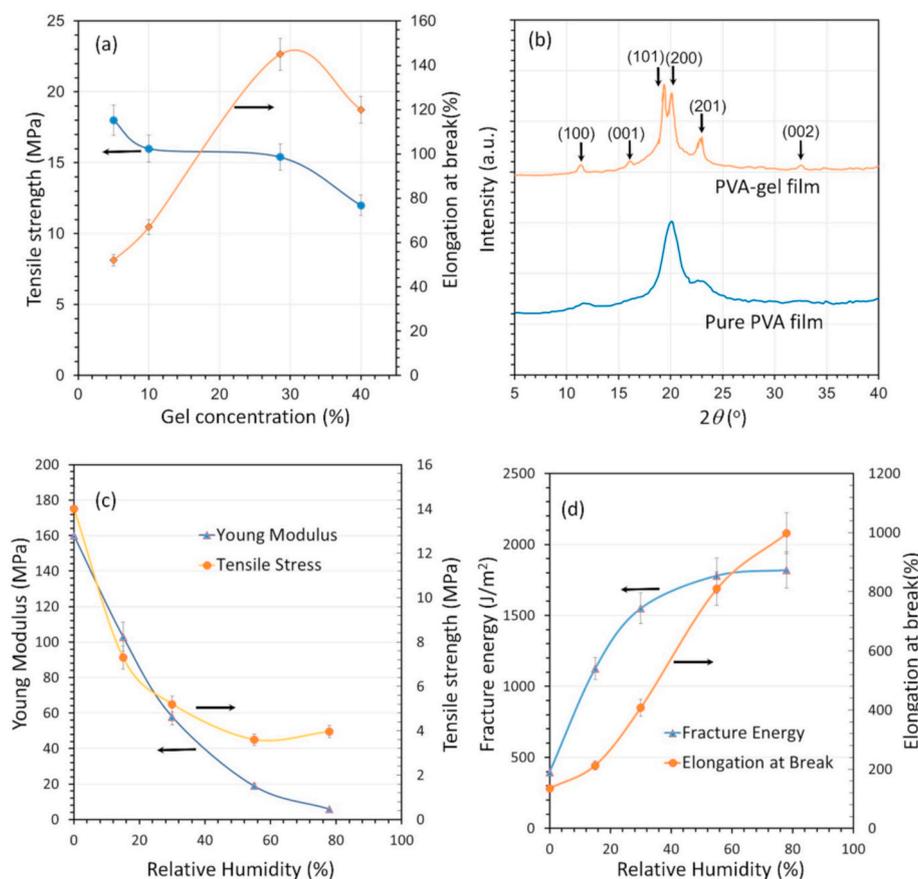


Fig. 5. (a) Changes in mechanical properties of PVA film as a function of gel concentration at 5% RH conditions; (b) the XRD patterns of pure PVA film and the PVA film with 28.6 wt% gel as plasticizer. Films were cast from water solutions; (c) effect of percent RH on the tensile modulus and strength of PVA film with 28.6 wt% gel and (d) effect of percent RH on the elongation at break and fracture energy of PVA film with 28.6 wt% gel.

change the tensile strength but improved the elongation value to about 150%. That is why this combination was chosen to produce the films for further testing including the antioxidant and oxygen gas barrier performance.

The XRD patterns for pure PVA and PVA-gel film (with 28.6 wt% plasticizers) are shown in Fig. 5b. Pure PVA exhibited two diffraction peaks at 20.17 and 22.96 that are attributed to the (101) and (200) crystal planes. When modified with the gel, the peak at 20.17 was split into two peaks at 19.20 and 19.80, and the intensity of the split peaks decreased. This indicates an increase in amorphous domains. New diffraction peaks were also measured at 18, 23 and 34, suggesting a new polymorph. This suggests that the glucose and sugar induced a heterogeneous nucleation effect indicating that the distribution of the crystalline grains was homogeneous and the amount of grains with the same polymorph increased, which is commonly seen in polyol plasticized polymers (Wu et al., 2012). To study the effect of moisture on the mechanical properties of the films, the film with 28.6 wt% gel was chosen. Its Young's modulus, tensile strength, fracture energy and elongation at break values were measured between 0% and 78% RH. As can be seen in Fig. 5c and d, water absorption causes a plasticization effect in the films as both PVA and carrageenan are hygroscopic polymers. Increasing RH, decreased the elongation modulus (Fig. 5c) and tensile strength but increased elongation at break and fracture energy values (Fig. 5d), respectively. This is attributed to increased molecular and polymeric chain mobility due to absorbed water molecules (Vieira et al., 2011).

3.5. Antioxidant activity, water uptake and oxygen barrier properties of the films

Carminic acid (7- β -D-glucopyranosyl-9,10-dihydro-3,5,6, 8-

tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylic acid) is the main component of the cochineal food dye obtained from the insect *Dactylopius coccus* (Li et al., 2009). Carminic acid has a number of biological activities. It can inhibit ascites tumors because its chemical structure is very similar to shikonin and anthracyclines are used as antitumor drugs. Carminic acid does not seem to have the toxicity problems associated with those drugs. In addition, studies on the reactions of carminic acid with 2,2'-diphenyl-1-picrylhydrazyl (DPPH) (Jiménez-Escrig et al., 2000) and 2,2'-azinobis (3-ethylbenzothiozoline-6-sulfonate) radical cation (ABTS⁺) (Erel, 2004) demonstrated direct evidence for carminic acid to scavenge radicals. In this work, we also measured the strong scavenging effect of carminic acid released from non-plasticized (with carminic acid) and gel plasticized PVA films as shown in Fig. 6.

It was effective against both DPPH and ABTS⁺, particularly as its concentration was increased for 36 h. Films plasticized with the gels had higher percent inhibition and at the end of 30 h against both DPPH and ABTS⁺ stabilizing at 98% and 87%, respectively (see Fig. 6b). Contrarily, PVA films containing the same amount of carminic acid but no gel showed 70% and 85% inhibition levels against DPPH and ABTS⁺, respectively (see Fig. 6a). Similar films containing no carminic acid demonstrated negligible to low inhibition levels. Pure PVA, for instance, inhibit only 20% of both DPPH and ABTS⁺ that confirms earlier observations (Singh et al., 2018); whereas, PVA films with gels without carminic acid had slightly higher inhibition effect at 30%. This may be attributed to the inherent antioxidant activity of carrageenan in the gels (Yuan et al., 2005). Since carrageenan is not easily soluble in water as carminic acid its release into the medium from the films is much slower than carminic acid but more importantly it has been shown that sugars interact with carrageenan polymeric chains by binding and this might

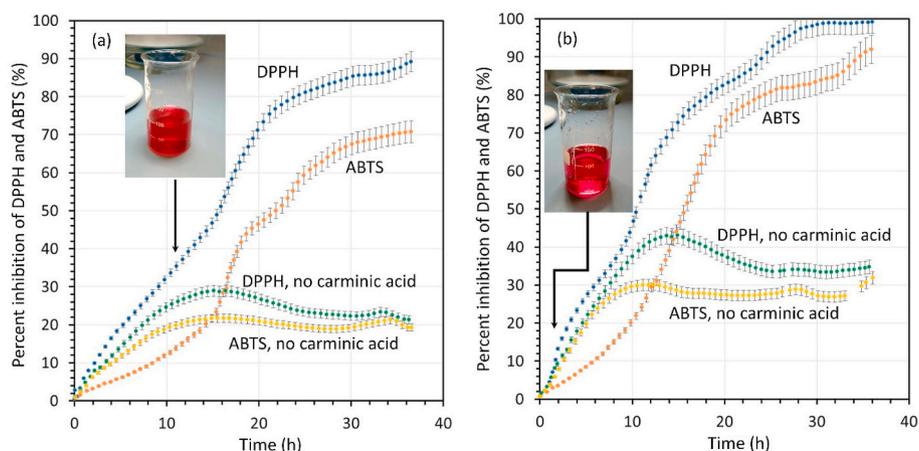


Fig. 6. (a) Percent inhibition of DPPH and ABTS based on carminic acid release from pure PVA films. The inset is a photograph of a beaker containing 100 mL water and 1.5 g pure PVA film from which carminic acid was released after 10 h. (b) Percent inhibition of DPPH and ABTS based on carminic acid release from PVA-gel films. The inset is a photograph of a beaker containing 100 mL water and 1.5 g of PVA-gel film from which carminic acid was released after 2 h.

also modify the antioxidant activity of carrageenan (Stenner et al., 2016). Although this is beyond the scope of this work, it will be investigated in more detail as future work.

Percent water uptake of pure PVA and PVA-gel films are shown in Fig. 7a, as a function of relative humidity. Naturally, due to their hydrophilicity, both films uptake more water as the percent humidity is increased. Gel plasticized (gel modified) films appear to show slightly higher water uptake values up until 85% relative humidity, which might be due to the plasticization effect and increased inter-chain polymer mobility (Quilez-Molina et al., 2020). PVA is one of the most effective barrier polymers against oxygen gas transmission particularly under low relative humidity conditions (Maes et al., 2018). However, there are other non-biodegradable commercial packaging films that are made in multilayers such as ethylene-vinyl copolymers with PET that are better than PVA. Improving PVA oxygen gas barrier properties by antioxidants can make it more competitive and perhaps more cost effective against other flexible multilayer packaging films (Bayer, 2021a,b).

We also measured very low oxygen permeation (OP) values (about $4.0 \text{ cm}^3 \mu\text{m}^2 \cdot \text{day} \cdot \text{atm}$) for both pure PVA film and the PVA-gel films. However, as the gel (plasticizer) concentration exceeded 28.6%, the OP value increased to levels above $10 \text{ cm}^3 \mu\text{m}^2 \cdot \text{day} \cdot \text{atm}$. Since carminic acid is an antioxidant, it might chemically scavenge oxygen within the films. To test this hypothesis, we also measured OP of PVA-gel films that

did not contain carminic acid (PVA-gel-NCA). As seen in Fig. 7b, indeed the average OP value is about $7.0 \text{ cm}^3 \mu\text{m}^2 \cdot \text{day} \cdot \text{atm}$ compared to $3.4 \text{ cm}^3 \mu\text{m}^2 \cdot \text{day} \cdot \text{atm}$ which was almost halved by the presence of carminic acid that is known to scavenge reactive oxygen species (Kang et al., 2013). Recently, some promising natural films with antioxidant properties have been published demonstrating good OP values (Jouki et al., 2013, 2014). These films generally display OP values of the order of $40.0 \text{ cm}^3 \mu\text{m}^2 \cdot \text{day} \cdot \text{kPa}$. In kilopascals, pure PCL film is about $100 \text{ cm}^3 \mu\text{m}^2 \cdot \text{day} \cdot \text{kPa}$ and our OP values are around $0.1 \text{ cm}^3 \mu\text{m}^2 \cdot \text{day} \cdot \text{kPa}$. This is due to the superior vinyl polymer chemistry that endows PVA an exceptional OP performance. However, the aforementioned natural films performance much better than biodegradable polyesters such as PCL.

Although PVA has good gas barrier properties, these properties diminish very quickly upon water or moisture uptake from the ambient due to its inherent hydrophilicity. Its mechanical properties also change significantly upon interaction with moisture and water. To reduce or eliminate these problems, PVA films can be protected by laminating with other hydrophobic biopolymers (Kim et al., 2018). The PVA-gel films were laminated between two PCL films by hot-pressing at $80 \text{ }^\circ\text{C}$, as seen in Fig. 7b. Although PCL is a flexible and hydrophobic polymer, it has a very poor OP value of about $96500 \text{ cm}^3 \mu\text{m}^2 \cdot \text{day} \cdot \text{atm}$ (Myllymäki et al., 1998), as seen in Fig. 7b. It has been implemented in

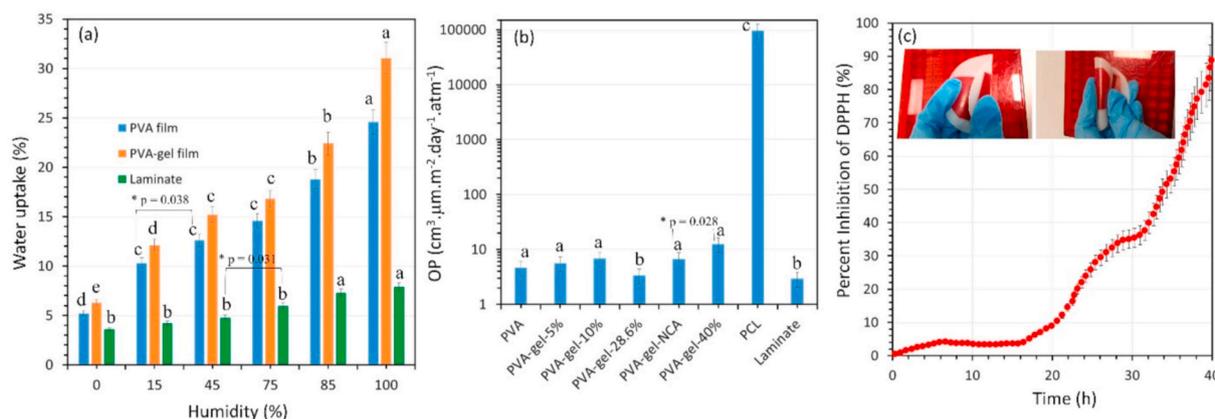


Fig. 7. (a) Percent water uptake values of pristine PVA and PVA-gel films as a function of percent humidity within the conditioning chamber. (b) Measured oxygen permeation (OP) values of various films including the PVA-gel film (28.6% gel) sandwiched between PCL films. PVA-gel-NCA designates gel-modified film without carminic acid. The inset photographs show that the laminate or the sandwiched film is very flexible. Note that a, b, c and d are different letters corresponding to significant differences ($p < 0.05$) between the means obtained in Duncan's test. (c) DPPH percent inhibition due to carminic acid release from PCL laminated PVA-gel film containing 28.6 wt% gel.

multilayer or bilayer films with natural polymers like chitosan (Sogut and Seydim, 2019). Once a layer of PVA-gel is sandwiched between PCL films, the resulting multilayer film demonstrates an OP value of $3.0 \text{ cm}^3 \mu\text{m}^2 \cdot \text{day} \cdot \text{atm}$, which is as low as PVA itself with added hydrophobicity of the PCL. Indeed, the percent water uptake of the laminate was also much lower compared to the PVA based films as seen in Fig. 7a. Fig. 7c shows that the thermal PCL lamination does not degrade the antioxidant potency of the PVA-gel film with 28.6 wt% gel content. However, compared to the results shown in Fig. 6, DDPH inhibition process of the laminated films (Fig. 7c) are much slower and becomes effective after about 20 h. This is expected since PCL resists erosion in solution and slows down the release of carminic acid from the middle section of the laminate. As a result, these gel-modified PVA films with good antioxidant and radical scavenging activities can be used to improve oxygen barrier properties of other thermoplastic polymers with poor barrier properties such as PCL with direct implications in bio-based and biodegradable multilayer food packaging (Bayer, 2021a,b; Quilez-Molina et al., 2021). Aside from improving PCL barrier properties, PCL is a hydrophobic polymer and can prevent moisture-induced changes in the PVA-gel film properties by covering their surface as thin film coating. Further systematic work will be conducted to characterize these laminates in full detail.

3.6. PVA-gel film color changes when exposed to NH_3 vapors

Carminic acid color changes are strongly pH-sensitive. At pH values below 4.5, it appears pale orange; at pH 7–7.7 light red and red, and at pH above 10, its color is magenta-red (Müller-Maatsch and Gras, 2016). The color changes of the PVA-gel film are presented in Fig. 8. Note that as control tests, pure PVA film modified only with the carminic acid corresponding to the same carminic acid concentration in the PVA with 28.6 wt% gel films was also exposed to the ammonia vapors and had exactly the same color response (see Fig. 8a and b). As such, the other ingredients of the gel did not diminish the response of carminic acid. After 1 min of exposure to NH_3 vapors, PVA-gel film changes its color (Fig. 8a) and intensity of the color change increases with an increase in the exposure time to NH_3 vapors. This was quantified by the CIELab analysis (Fig. 8b) that shows an increase in the ΔE value with time from 3.6 to 19.4 (after 1–15 min of exposure to NH_3 vapors). The PVA-gel film shows a ΔE value of 3.6 just after 1 min of exposure to NH_3 vapors, indicating that the color change is perceivable by the naked eye. The color changes are in accordance with the UV visible spectra of the

PVA-gel film. As shown in Fig. 8c and d, the characteristic peak of the carminic acid in the visible region at 491 nm disappears and a new peak appears around 380 nm just after 1 min's exposure to NH_3 vapors and intensity of the color increase with an increase in the reaction time to the NH_3 vapors indicating pH sensing ability of the carminic acid towards basic vapors. Furthermore, other characteristic peaks of the PVA-gel film e.g. 521 nm and 561 nm also shifted to 540 nm and 581 nm, respectively just after 1-min exposure to NH_3 vapors followed by an increase in the intensities of the peaks in time, demonstrating the ammonia sensing ability of the PVA-gel film. The basic vapor sensitivity of the PVA-gel film can be beneficial to monitor the freshness of the meat and seafood products for the crucial supply chain (Zia et al., 2021; Quilez-Molina et al., 2021).

4. Conclusions

Polyvinyl alcohol, PVA, films lack plasticity and lose their mechanical and gas barrier properties over time due to their sensitivity to atmospheric moisture uptake. To circumvent this problem, we proposed plasticizing PVA with an edible gel containing a natural antioxidant, carminic acid. Glucose and sugars in the gel enabled PVA films to be a lot more flexible compared to pure PVA with elongation at break value of about 150% and a tensile strength of 15 MPa. The optimum polymer: gel blend ratio was 1:1 corresponding to 28.6 wt% sugars in PVA as a plasticizer. Gel-modified PVA films had very low oxygen permeation value (OP, $3.4 \text{ cm}^3 \mu\text{m}^2 \cdot \text{day} \cdot \text{atm}$), which was partially assisted by the presence of carminic acid, a known oxidative radical scavenger. When immersed in aqueous or ethanol solutions, the films released carminic acid in a sustained fashion and at the end of 36 h, the released carminic acid demonstrated a strong inhibition effect against standard stable free-radical molecules known as DPPH and ABTS^{•+}. Finally, the gel-modified films were sandwiched between two hydrophobic polycaprolactone (PCL) films by hot pressing to protect them from the effects of atmospheric moisture or direct contact with water by a simple lamination process. The resultant laminates were hydrophobic and flexible and maintained low levels of oxygen permeation. We showed a simple processing method to obtain plasticized PVA films with good mechanical properties and low oxygen permeation values ideal for food protection. Moreover, they could be laminated into hydrophobic bio-based polyesters to serve as more sophisticated food preservation multilayer films. The films also changed color from red to magenta upon exposure to ammonia vapors that can further increase their potential use as food

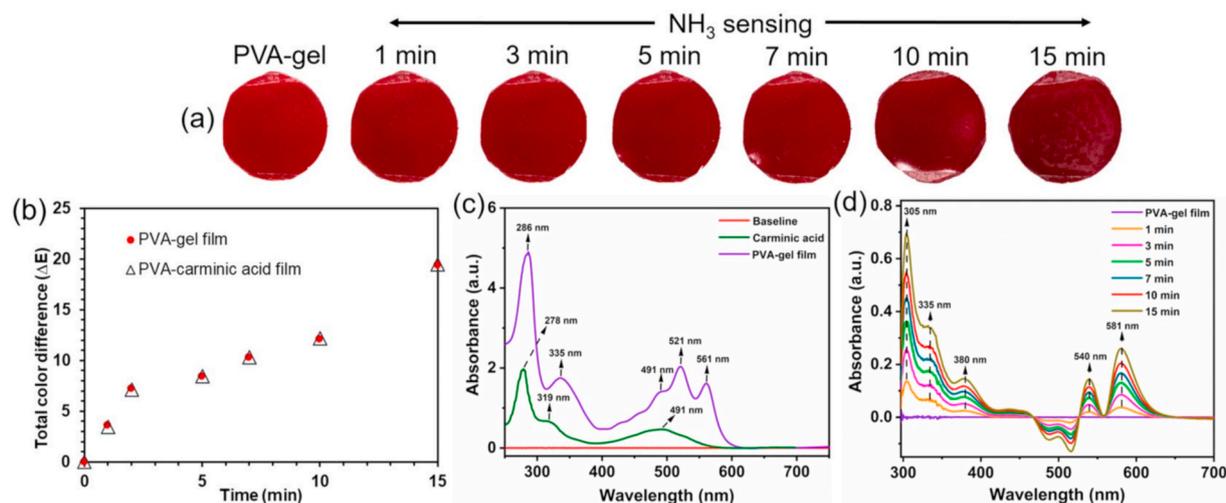


Fig. 8. a) Color changes of the PVA-gel film upon exposure to NH_3 vapors. (b) CIELab color analysis of the PVA-gel film and pure PVA containing only carminic acid (c) Absorption spectra of carminic acid solution and PVA-gel film. (d) Corresponding absorption spectra of the color changes of the PVA-gel film upon exposure to NH_3 vapors. For background correction, PVA-gel film was used in Fig. 8d. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

spoilage indicators. Modifying aqueous polymer solutions with functional gels can prevent excessive solvent/water use and subsequent water elimination without disrupting mixture viscosity as gels contain much less water. This work may pave the way for using many other edible gels that contain natural antioxidant molecules such as polyphenols to functionalize and modify polyvinyl alcohol for food packaging applications.

Credit author statement

G. Bayer: Methodology, Data curation, Formal analysis, Visualization. **A. Shayganpour:** Methodology, Data curation, Formal analysis, Visualization. **J. Zia:** Methodology, Data curation, Formal analysis, Visualization, Writing. **I. S. Bayer:** Conceptualization, Investigation, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jfoodeng.2022.111000>.

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