

Performance of photo-curable metal-chelating active packaging coating in complex food matrices

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ABSTRACT

Many packaged goods undergo transition metal-catalyzed oxidative spoilage. Recently, a nonmigratory photo-curable metal-chelating coating was developed as an innovative active packaging approach to control oxidation of foods. In the present study, we investigate the influence of competing ions and increasing viscosity on the iron-chelating capacity and antioxidant efficacy of this coating in a model complex food system. The addition of calcium and magnesium causes a decrease in iron chelating capacity; however, 61% chelating capacity of materials was retained when 0.8 M sodium was present. Materials retained iron-chelating capacity even in solutions of 2700 cP, similar to the viscosity of salad dressing. Additionally, metal-chelating films significantly delayed transition metal-catalyzed ascorbic acid degradation, even in the presence of competing ions and at increased viscosity. These results suggest that metal-chelating active packaging coatings may present a new technological approach to addressing consumer demands for reduced additive use while controlling food spoilage and waste.

1. Introduction

Oxidative degradation catalyzed by transition metals (e.g. iron, copper) is a significant issue in the food industry (Logan, Nienaber, & Pan, 2013). It can cause a loss in nutritional quality of foods as well as quality deterioration such as discoloration and the generation of rancid off-flavors in many packaged foods during transportation and storage (Decker, Elias, & McClements, 2010). Indeed, even trace amounts of iron can initiate oxidation of labile molecules including unsaturated fatty acids, natural colors and essential amino acids (Goddard, McClements, & Decker, 2012). To prevent spoilage and extend shelf life, synthetic metal chelators such as ethylenediaminetetraacetic acid (EDTA) are often added to packaged foods to inhibit such oxidative reactions. However, as consumers are increasingly demanding cleaner label products with reduced additive use, alternative preservation technologies are needed (Bearth, Cousin, & Siegrist, 2014).

One strategy for maintaining product quality and shelf life is the design of active packaging technologies (Bastarrachea, Wong, Roman, Lin, & Goddard, 2015; Lee et al., 2018; Lin, Decker, & Goddard, 2016; Lorenzo, Batlle, & Gómez, 2014). The traditional role of packaging in preserving food quality by providing containment and protection against environmental influences (e.g. oxygen, light, dust, contamination). Packaging therefore plays a role in reducing food waste from field to fork (Wikström, Williams, Verghese, & Clune, 2014). To address

demands for cleaner labels, non-migratory metal-chelating active packaging materials have been developed, with the goal of removing EDTA without compromising the product quality and shelf life. In this type of active packaging, chelating ligands are immobilized onto the surface of traditional packaging materials via a covalent linkage (rendering it unlikely to migrate to the product) with retention of chelating capacity (Lin, Roman, Decker, & Goddard, 2016; Tian, Decker, & Goddard, 2013). Such active packaging technology may thus enable retention of product quality and shelf-life even after removal of synthetic chelators.

In another report on metal-chelating active packaging, poly-hydroxamic acids served as the chelating ligand, and it was found that materials exhibited more than 76% of the original metal-chelating capacity at viscosities of 10^4 mPa-s, similar to that of mayonnaise (Roman, Decker, & Goddard, 2015), and also retained chelating capacity in the presence of competing ions typical in foods and beverages (Ogiwara, Roman, Decker, & Goddard, 2016).

Recently, our research group reported on a new method to synthesize a latex poly (*n*-butyl acrylate) based copolymer via emulsion copolymerization with iminodiacetic acid (IDA) as metal-chelating ligand and benzophenone as photo-cross-linker (Lin & Goddard, 2018b). The copolymer coating technology enabled scalable preparation of chelating materials via a coat/cure process, using a chelating ligand (IDA) with a high affinity for common transition metals (e.g. iron and copper)

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and low affinity for desired minerals (e.g. sodium, calcium and magnesium) (Martell & Robert, 1974). The efficacy of this coating in chelating iron and controlling ascorbic acid degradation was demonstrated in buffered, acidic aqueous environments (pH 3.0 and 5.0) (Lin & Goddard, 2018a, 2018b; Lin et al., 2016). However, its performance in complex conditions typical of food systems (e.g. presence of competing ions and high viscosity) has not yet been shown.

In this study, we analyzed the influence of calcium, magnesium, and sodium and increasing viscosities on the iron chelating capacity and antioxidant performance of a photocured metal-chelating copolymer coating presenting iminodiacetic acid (IDA) chelating ligands. Additionally, the ability of the metal-chelating film to control ascorbic acid degradation in the presence of competing ions and increasing methylcellulose (MC) concentration was also determined. It was hypothesized that the IDA functionalized copolymer coating would retain metal-chelating and antioxidant efficacy even in the presence of competing ions and increasing viscosities.

2. Materials and methods

2.1. Materials

Iminodiacetic acid (IDA) (98 + %) was purchased from Acros Organics (Morris Plains, NJ). Polypropylene pellets (isotactic, Cat# 130) were purchased from Scientific Polymer Products (Ontario, NY). Isopropanol, acetone, hydrochloric acid (trace metal grade), sodium acetate trihydrate, ferric chloride hexahydrate, and ethylenediaminetetraacetic acid (EDTA) (disodium salt dihydrate) were purchased from Fisher Scientific (Fair Lawn, NJ). 2,6-dichloroindophenol sodium salt hydrate, *n*-butyl acrylate (99 + %), potassium persulfate (99 + %), L-ascorbic acid, imidazole, sodium chloride, oxalic acid, methylcellulose (MC), magnesium chloride hexahydrate, and calcium chloride dihydrate were purchased from Sigma-Aldrich (St. Louis, MO). Absolute ethanol was purchased from Pharmco-Aaper (Brookfield, CT). Nitric acid (trace metal grade) was purchased from VWR Chemicals (Radnor, PA). 2-propenoic acid, 2-methyl-3-[bis-(carboxymethyl) amino]-2-hydroxypropyl ester (GMA-IDA) and 4-benzoylphenyl methacrylate (BPM) were synthesized according to the reported methods (Chuh-Yean & Chuh-Yung, 2002; Lin & Goddard, 2018b; Schlemmer, Betz, Berchtold, R  he, & Santer, 2009). All reagents were used as received.

2.2. Metal-chelating film synthesis

To prepare polypropylene films, polypropylene pellets were washed by sonication in isopropanol, acetone, and deionized (DI) water for two times and dried in a desiccator (20 °C, 15% relative humidity). Clean pellets were hot pressed (Carver Laboratory Equipment, Model #3925, Carver Inc., IN) at 200 °C, 9000 lbs. force. The resulting films were cut into 5 × 5 cm² pieces, cleaned and dried as described for pellet cleaning. The photo-curable metal-chelating copolymer was synthesized by emulsion copolymerization of GMA-IDA, *n*-butyl acrylate and BPM monomers as previously reported (Lin & Goddard, 2018b). Briefly, GMA-IDA, potassium persulfate, water, BPM, and *n*-butyl acrylate were introduced into a reaction vessel and purged with nitrogen gas with stirring for 20 min. After heating to 70 °C, the reaction continued with stirring for 20 h without exposure to light to produce the final copolymer, poly (2-propenoic acid, 2-methyl-3-[bis-(carboxymethyl) amino]-2-hydroxypropyl ester-*co*-*n*-butyl acrylate-*co*-4-benzoylphenyl methacrylate) (GMA-IDA-*co*-BA-*co*-BPM, referred to from here as ‘metal-chelating copolymer coating’). Crude emulsion copolymer was purified by centrifugation and dialysis in DI water, followed by dialysis in methanol. Dialysis was conducted using a 20 kDa regenerated cellulose membrane. The copolymer emulsion was stored in methanol at 4 °C until use. Metal-chelating films were prepared in a coat-cure method, as illustrated in Fig. 1. Emulsion copolymer (0.7 mL) was deposited onto the surface of polypropylene coupons. After methanol

evaporated, the coating was photocured under UV light (365 nm, ~205 mW/cm², Dymax 5000-EC Series, Torrington, CT) for 270 s. Metal-chelating films were washed three times in water (30 min, 60 °C) to remove residual monomers and loosely adsorbed oligomers and dried in a desiccator. The resulting metal-chelating films were cut into 1 × 2 cm² for further analysis.

2.3. Characterization of material surface morphology & chemistry

Surface morphologies of native polypropylene and metal-chelating copolymer coating were characterized using scanning electron microscopy (SEM). Samples were gold sputter-coated (108 auto, Model No.7002-8, Ted Pella Inc, Redding, CA) and imaged at 15 kV (JEOL, JCM 6000, Tokyo, Japan). Reported micrographs are representative of eight images in total (two images on each of four independently coated films). The surface chemistries of native polypropylene and metal-chelating copolymer coating were analyzed via attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (IRTracer-100, Shimadzu Corporation, Kyoto, Japan) using a diamond ATR crystal and a resolution of 4 cm⁻¹ (32 scans). Reported spectra are representative of spectra acquired on quadruplicate films with air as background.

2.4. Determination of metal-chelating capacity in complex systems

The iron chelating capacity of the metal-chelating copolymer coated films was determined by inductively coupled plasma-mass spectroscopy (ICP-MS) using a modification of a previously reported method (Lin & Goddard, 2018b). Briefly, native polypropylene and metal-chelating coated films were incubated in 0.08 mM ferric chloride solution in 50 mM sodium acetate/imidazole buffer at pH 4.0 in the dark for 96 h. After rinsing with absolute ethanol, films were dried under pressurized house air then dried in a desiccator. Two pieces of 1 × 2 cm² films (approximately 90 mg) were added to microwave digestion vessels (high purity TFM Teflon vessels, Milestone S.r.l., Sorisole, Italy). Films were digested in 5 mL of nitric acid (trace metal grade) using the Ethos Microwave Digestion Labstation (Milestone S.r.l., Sorisole, Italy) (ramp to 210 °C [20 min]; hold at 210 °C [20 min]; cool down). Digested samples were diluted with DI water to 50 mL and analyzed using ICP-MS on a Thermo Scientific Element 2 Series (Thermo Fisher Scientific, Waltham, MA). Iron chelation capacity was determined by comparison to ICP-MS iron calibration standards (Sigma-Aldrich, St. Louis, MO). The performance of the metal-chelating coating under conditions of competing ions typical in foods and beverages was characterized by addition of 35 mM CaCl₂, 10 mM MgCl₂, or 0.8 M NaCl to the ferric ion solution. These ionic concentrations were selected to represent those typical of milk, hard water, and salad dressing for calcium, magnesium, and sodium, respectively. The performance of the metal-chelating coating under conditions of increasing viscosity was characterized by adding the following concentrations of methylcellulose to the Fe³⁺ solution (0.08 mM ferric chloride in 0.05 M sodium acetate/imidazole, pH 4.0): 0.25%, 0.5%, 1%, or 2% (Roman et al., 2015). The viscosity of each concentration of methylcellulose was measured with a Brookfield DV1 Digital Viscometer (Middleboro, MA), and concentrations were selected to simulate viscosities similar to orange juice (Vitali & Rao, 1984), tomato juice, tomato sauce (Mirondo & Barringer, 2015) and salad dressing (Franco, Guerrero, & Gallegos, 1995), respectively.

2.5. Ascorbic acid degradation

Metal-chelating films were further studied for their ability to inhibit oxidative degradation of ascorbic acid. Coupons of metal-chelating films (1 cm²) were stored in 10 mL sealed gas chromatography vials with 1 mL of 20 mM ascorbic acid in 10 mM sodium acetate/imidazole buffer at pH 4.0 at 37 °C for 16 days without rotation, with blank ascorbic acid solutions, solutions incubated with native polypropylene,

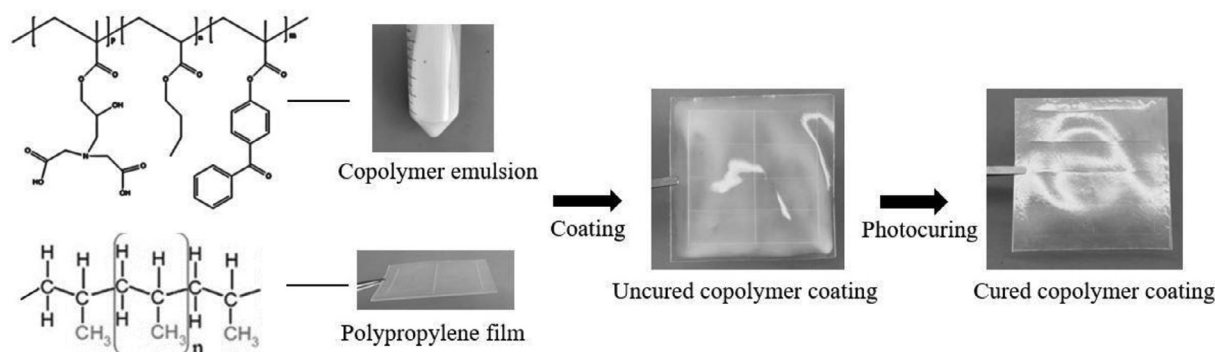


Fig. 1. Preparation of non-migratory metal-chelating active packaging coating. Copolymer emulsion, poly (2-propenoic acid,2-methyl-3-[bis-(carboxymethyl) amino]-2-hydroxypropyl ester-co-*n*-butyl acrylate-co-4-benzoylphenyl methacrylate) (GMA-IDA-co-BA-co-BPM), is coated onto polypropylene films followed by photocuring.

and solutions containing 0.08 mM EDTA (23.4 ppm equivalent, molecular weight 292.2 g/mol) as controls. According to Title 21 of the CFR, maximum permissible concentration of EDTA in salad dressing and sauces is 75 ppm; 33 ppm EDTA is the limit for carbonated soft drinks and alcoholic beverages (FDA, 2017). Ascorbic acid contents of solutions were determined by a modified dichloroindophenol assay (Association of Official Analytical Chemists 967.21) with slight modification (Horwitz, 1970; Lin et al., 2016). Briefly, 0.2 mL of the ascorbic acid solution was added to 4.8 mL of 0.04 wt% oxalic acid in water and mixed well. 0.9 mL aliquot of the mixture was mixed with 4.1 mL of 0.2 mM 2,6-dichloroindophenol in water, resulting in a color change in the solution. Absorbances were measured at 520 nm immediately (Synergy Neo2 Hybrid Multi-Mode Reader, BioTek Instruments, Winooski, VT) and compared to ascorbic acid standards in 10 mM sodium acetate/imidazole buffer at pH 4.0 to determine ascorbic acid content. Ascorbic acid degradation half-life and rate coefficients were determined by fitting data to a first-order degradation rate equation. The influence of competing ions on antioxidant efficacy of metal-chelating films was characterized by addition 35 mM CaCl_2 , 10 mM CaCl_2 , 10 mM MgCl_2 , 10 mM NaCl or 0.8 M NaCl to the ascorbic acid solutions. The effect of viscosity on the antioxidant efficacy of the metal-chelating films was determined by addition of methylcellulose to the ascorbic acid solution at concentrations of 0.25%, 0.5%, 1%, or 2%. Films were submerged in 1 mL of each ascorbic acid solution and incubated at 37 °C for 7 days without rotation. Ascorbic acid contents were measured on day 0 and day 7 to determine ascorbic acid retention under simulated complex food matrix conditions using the dichloroindophenol assay as described above.

2.6. Statistics

The preparation of metal-chelating films was conducted in duplicate batches and all reported results are representative of at least two experiments performed on independent days. Unless otherwise noted, characterizations were performed using quadruplicate samples of metal-chelating films prepared from the same batch of copolymer emulsion. Means from analysis of variance (ANOVA) analysis were compared using Tukey's multiple comparison tests ($P < 0.05$) in GraphPad Prism 6.0 (La Jolla, CA). First order degradation kinetics of ascorbic acid degradation were calculated in GraphPad Prism 6.0.

3. Results and discussion

3.1. Surface characterization

The metal-chelating copolymer latex coating was cast onto the surface of polypropylene and formed a clear and glossy cured coating after photocuring under UV-light. The surface morphologies of the

native and metal-chelating films were observed under SEM (Fig. S1A and B). Compared to the smooth surface of native polypropylene, the metal-chelating coating presented a slight increase in surface roughness on its uniform morphology. ATR-FTIR spectroscopy was used to characterize the surface chemistries of the metal-chelating and the control sample native polypropylene (Fig. 2). Native polypropylene showed characteristic absorption bands at 3000–2800 and 1500–1400 cm^{-1} , typical of alkane stretching and bending vibrations, respectively. Metal-chelating films exhibited strong absorbances at 1730 and 1240 cm^{-1} , representing the C=O and C–O–C stretching vibrations, respectively. The small band at 1637 cm^{-1} represented deprotonated IDA ligands, indicating successful introduction of IDA ligands (Lin & Goddard, 2018a; Lin et al., 2016). These absorption bands are characteristic for the metal-chelating materials and in agreement with prior reports (Misra, Pichot, El-Aasser, & Vanderhoff, 1983; Suma, Jacob, & Joseph, 2010).

3.2. Influence of competing ion and viscosity on metal chelation

The iron chelating capacity of the metal-chelating material was quantified by analyzing the Fe^{3+} content of the films after storage in ferric buffered solutions for 96 h, using ICP-MS in the digest of the coated films ($1 \times 2 \text{ cm}^2$). Metal-chelating films prepared using 28 $\mu\text{L}/\text{cm}^2$ of copolymer emulsion presented a ferric iron chelating capacity of $95.6 \pm 17.0 \text{ nmol}/\text{cm}^2$ at pH 4.0 while uncoated polypropylene bound only trace ($4.3 \pm 0.7 \text{ nmol}/\text{cm}^2$) ferric ion, likely due to iron precipitation or equipment sensitivity. These results suggest that native polypropylene does not adsorb significant amounts of iron and that the

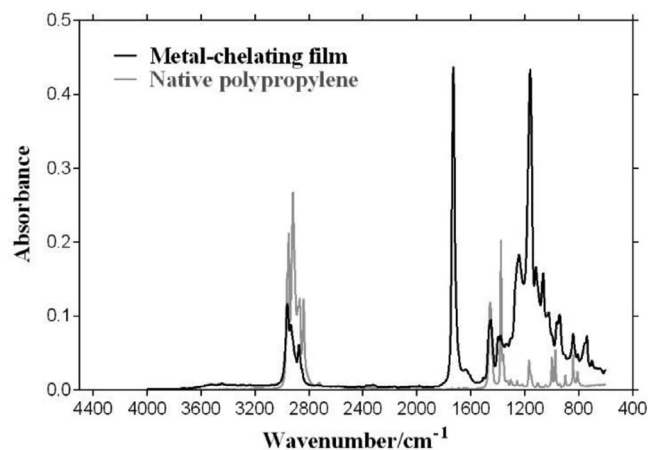


Fig. 2. ATR-FTIR spectra of native polypropylene and metal-chelating film. Each spectrum is representative of a total of four spectra collected on quadruplicate samples.

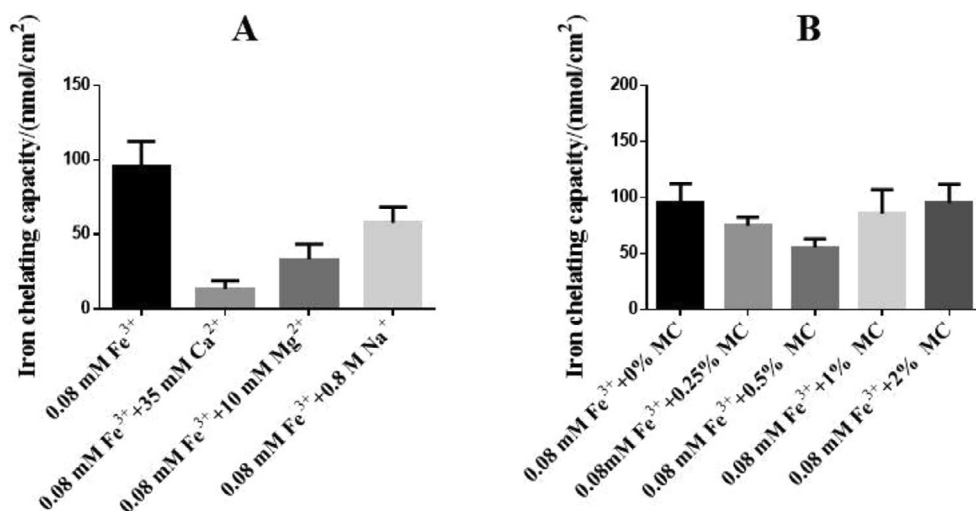


Fig. 3. Effect of competing ions (A) and viscosity (B) on the iron chelating capacity of metal-chelating films. Viscosity was modified by the addition of methylcellulose (MC). Values are means with error bars representing standard deviation ($n = 4$).

observed metal chelation on the coated film is due to the interactions that are ligand-specific. The effect of competing ions and increasing viscosity on the metal-chelating activity at pH 4.0 was further analyzed (Fig. 3A and B). The amount of Fe³⁺ chelation decreased significantly in the presence of 35 mM Ca²⁺ or 10 mM Mg²⁺, which might be explained by the stability constants of IDA for different ions. IDA has higher stability constants for Fe³⁺ ($\log K = 10.7$) and Cu²⁺ ($\log K = 10.6$), and lower affinity for other ions common in foods, such as Ca²⁺ ($\log K = 2.6$), Mg²⁺ ($\log K = 3.0$), and Na⁺ ($\log K = 0.4$), calculated at an ionic strength of 0.100 M and 25 °C (Martell & Smith, 1974). Nevertheless, metal-chelating film still retained 14% and 35% chelating capacity for calcium and magnesium, respectively. In term of sodium, no significant difference in the amount of Fe³⁺ chelation was observed with the addition of 0.8 M Na⁺, as expected from the very low stability constant between IDA and sodium ions. To increase viscosity, the ferric solutions were thickened with 0.25%, 0.5%, 1% and 2% methylcellulose. The apparent viscosity was then measured by viscometer at 100 rpm at 20 °C (Fig. S2). According to statistical analysis, no significant difference between samples was observed despite the increase of viscosity up to 2% methylcellulose. It suggests that the active packaging material has the potential to be used viscous food and beverage systems as an alternative metal-chelating system to prevent transition metal-induced oxidations because it retains efficacy at viscosities up to 2700 cP (centipoise), the viscosity of 2% methylcellulose and similar to the viscosity of salad dressing.

3.3. Antioxidant efficacy

The antioxidant efficacy of the photocurable, metal-chelating coating was characterized by measuring its ability to hinder ascorbic acid oxidation at pH 4.0. The oxidative degradation of ascorbic acid can occur under both aerobic and anaerobic conditions and depends on factors such as temperature, pH, storage time and the presence of transition metals (Bosch et al., 2013). In aerobic degradation, L-ascorbic acid is oxidized to the labile dehydroascorbic acid (Peleg, Normand, Dixon, & Goulette, 2018). A storage study was performed in which metal-chelating films were stored in solutions of ascorbic acid at pH 4.0 and 37 °C, and ascorbic acid content was measured at each time point over 16 days (Fig. 4). The blank ascorbic acid solution, the ascorbic acid solution with native polypropylene, and the ascorbic acid solution containing EDTA were prepared as controls. The results showed that the ascorbic acid degradation of blank and polypropylene can be successfully described by a 2nd-order kinetics as limited oxygen is present in the vial (Baiano, Marchitelli, Tamagnone, & Nobile, 2004). However,

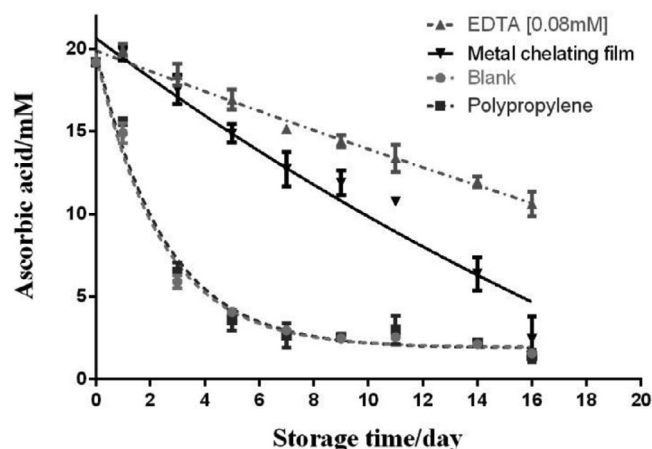


Fig. 4. Control of ascorbic acid degradation by metal-chelating films at pH 4.0 (stored at 37 °C) over 16 days. Values represent means with error bars indicating standard deviation ($n = 4$). In some instances, error bars are smaller than data points.

for ascorbic acid degradation of EDTA and metal-chelating film, a first-order model was followed as degradation was much slower and oxygen was not yet a constraint, in agreement with previous reports (Assiry, Sastry, & Samaranyake, 2006; Li, Yang, Yu, & Wang, 2016). At pH 4.0, ascorbic acid solution alone (negative control) and with native polypropylene exhibited identical degradation kinetics with a calculated shortest degradation half-life of 2 days, suggesting that native polypropylene has no effect on ascorbic acid. On the other hand, when incubated with metal-chelating films, degradation was significantly slowed, extending the degradation half-life to 10 days. EDTA showed the strongest efficacy in slowing down ascorbic acid degradation at pH 4.0 and retained about 50% of the ascorbic acid on day 16. These results are in agreement with prior reports which suggest that ascorbic acid degradation can be controlled by metal-chelating materials by scavenging transition metal ions (Lin & Goddard, 2018a, 2018b; Lin et al., 2016). These results suggest that while EDTA remains the most effective at controlling ascorbic acid degradation, the metal-chelating coating extended the degradation half-life from 2 to 10 days, indicating its potential to be used as an antioxidant active packaging material to inhibit the degradation of transition metal-catalyzed oxidation.

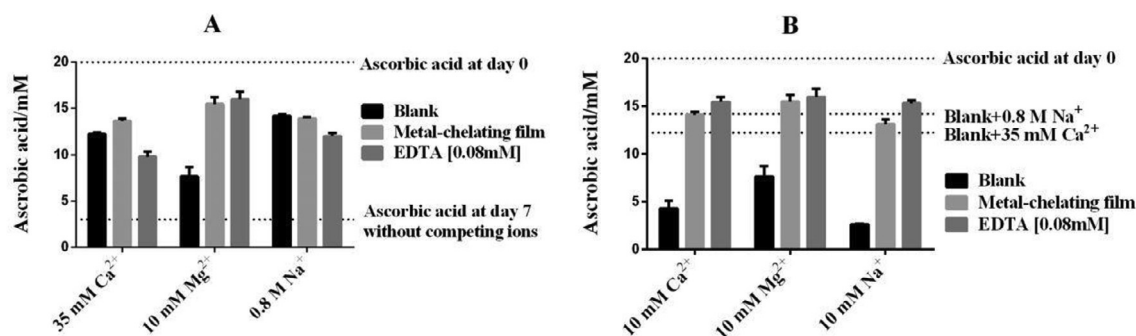


Fig. 5. Effect of high concentration (A) and low concentration (B) of competing ions (Ca^{2+} , Mg^{2+} , Na^{+}) on the metal-chelating films' ability to control ascorbic acid degradation after storing at 37 °C for 7 days. Values are means with error bars representing standard deviation ($n = 4$).

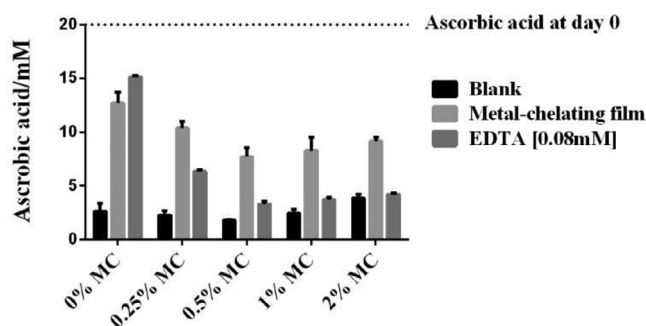


Fig. 6. Effect of viscosity on the metal-chelating films' ability to control ascorbic acid degradation after storing at 37 °C for 7 days. Viscosity was modified by the addition of methylcellulose (MC). Values are means with error bars representing standard deviation ($n = 4$).

3.4. Influence of competing ions on antioxidant efficacy

The influence of competing ions and viscosity on the antioxidant efficacy of metal-chelating films was determined by characterizing their influence on controlling degradation of ascorbic acid at 37 °C and pH 4.0 for 7 days. Ascorbic acid solutions containing 35 mM Ca^{2+} , 10 mM Mg^{2+} , and 0.8 M Na^{+} were prepared and the ascorbic acid contents on day 0 and day 7 were measured (Fig. 5A). In the blank solution (ascorbic acid solution without competing ions, EDTA, or metal-chelating film), there was a 85% reduction in ascorbic acid content after 7 days, while solutions containing 35 mM Ca^{2+} , 10 mM Mg^{2+} and 0.8 N Na^{+} (but no EDTA or chelating film) exhibited reductions of 39, 62, and 29%, respectively. These results are in agreement with previous reports which showed that sodium chloride (0.1 M) at pH 7.0 has an inhibiting effect on the oxidation of ascorbic acid by a hypothesized mechanism of inhibiting the catalytic power of copper (Høygaard & Rasmussen, 1938; Kellie & Zilva, 1935). Another study also found that by using an accelerated stability test, the addition of $\text{Mg}(\text{II})$ ions (1 mg/L) stabilizes ascorbic acid (0.3 mM) to a great extent (Dolińska et al., 2012). In another study, although not performed in aqueous solutions, calcium presence in edible films stabilized ascorbic acid and slowed down the browning development because of higher water immobilization (León, Lamanna, Gerschenson, & Rojas, 2008; Pérez, Fissore, Gerschenson, Cameron, & Rojas, 2012). The inhibiting phenomenon was further studied by reducing calcium and sodium to the same concentration of magnesium (10 mM) (Fig. 5B). After reducing the concentration of calcium chloride and sodium chloride, the ascorbic acid content on day 7 (without the chelating film or EDTA) sharply dropped to a similar level of that without competing ions (~4 mM, 80% reduction), confirming prior reports that regardless of controlling transition metal reactivity, competing ions can inhibit the degradation of ascorbic acid to certain degrees. Importantly, at both

lower and higher concentrations of sodium and calcium, the metal-chelating films were capable of controlling ascorbic acid degradation, exhibiting a retention of about 70% ascorbic acid after 7 days. These results support our original hypothesis that the reported metal-chelating films retain antioxidant efficacy in the presence of calcium, sodium, and magnesium. Interestingly, while the metal-chelating films retained their antioxidant activity, the higher concentrations of calcium and sodium (at levels typical of those found in milk/fortified beverages and salad dressings, respectively) reduced the efficacy of EDTA, which was less effective than the reported metal-chelating film under those conditions. These results are expected, as calcium and sodium can be chelated by EDTA, reducing its ability to control metal promoted ascorbic acid degradation. In summary, the reported photocurable, IDA copolymer coating was effective in controlling ascorbic acid degradation in the presence of competing ions (Ca^{2+} , Mg^{2+} , and Na^{+}), even at concentrations for which EDTA is less effective.

3.5. The effect of viscosity on antioxidant efficacy

The antioxidant performance of metal-chelating film at a series of viscosities thickened by methylcellulose was characterized by studying the ascorbic acid content remaining on day 7 (Fig. 6). Under blank conditions (ascorbic acid solution with neither chelating film nor EDTA), more than 80% ascorbic acid was degraded, with no statistical difference between different viscosity levels. The metal-chelating film retained more than 60% antioxidant efficacy at viscosities up to 2700 cP (2% methylcellulose). In contrast, while EDTA was effective in controlling ascorbic acid degradation in the absence of methylcellulose (~75% retention in ascorbic acid), it had reduced efficacy with increasing methylcellulose content. At methylcellulose concentrations of 0.5% and higher (corresponding to the thickness of tomato juice and thicker) the retention of ascorbic acid in the presence of EDTA after 7 days reduced from approximately 75–20%. In this study, the reported metal-chelating film outperformed EDTA in controlling ascorbic acid degradations under conditions of increasing viscosity, suggesting the potential of the reported photocured metal-chelating copolymer coating in controlling transition metal promoted oxidative degradation in complex food matrices.

4. Conclusion

In this work, we investigated the iron chelating capacity and antioxidant efficacy of a metal-chelating copolymer coating synthesized via emulsion polymerization and applied on polypropylene films by a coat/cure process. In the presence of 35 mM calcium and 10 mM magnesium, the iron chelating capacity of metal-chelating film was significantly reduced while the addition of 0.8 M sodium had no effect. Interestingly, under conditions of lower calcium and magnesium concentration, under which these ions have less of a protective effect towards ascorbic

acid, the metal-chelating films performed well in controlling ascorbic acid degradation, to a similar degree as EDTA. In addition, the metal-chelating film exhibited a high retention of antioxidant efficacy and controlled metal-induced ascorbic acid degradation even under conditions of moderate viscosity (2700 cP), significantly outperforming EDTA. In summary, the reported metal-chelating copolymer coating can be applied on common polymeric packaging materials by a simple coat/cure process with retention of iron chelating capacity and demonstrated antioxidant efficacy even in the presence of competing ions (calcium, magnesium, and sodium) and increasing viscosities. Such metal-chelating active packaging coating has the potential to substitute EDTA in foods with a high ionic composition or moderate viscosity, in support of on-going trends to reduce the use of additives in foods and beverages.

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Conflict of interest

The authors declare no competing financial interest.

Appendix A. Supplementary material

Raw data tables for are available as supplementary information. Raw FTIR spectral data are available upon request. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2019.01.195>.

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