


# Edible Polyelectrolyte Complex Nanocoating for Protection of Perishable Produce

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**ABSTRACT:** Approximately one-third of the food produced in the world is not consumed, largely due to spoilage. Fresh fruits and vegetables have a shelf life of only a few days. To reduce spoilage, packaging with a high oxygen barrier is needed, but plastic packaging also creates waste. In this study, edible polyelectrolyte complexes consisting of chitosan (CH) and pectin (PT) are deposited onto fresh fruit to extend shelf life. This unique edible coating imparts a high gas barrier and high transparency that can slow the ripening of bananas and browning of apple slices. A 1.5  $\mu\text{m}$  thick CH/PT coating reduces the oxygen transmission rate of a 179  $\mu\text{m}$  polyester film by >10-fold. This single-step deposition process uses only water-soluble, edible biopolymers and ambient conditions, which is promising for reducing both food and packaging waste.

**KEYWORDS:** *polyelectrolyte complex, food packaging, oxygen barrier, gas permeability, water-based*

## INTRODUCTION

World hunger is on the rise, with 800 million people suffering from food insecurity.<sup>1</sup> The Food and Agriculture Organization (FAO) of the United Nations reports that approximately one-third of the food produced worldwide is wasted (i.e., never consumed), which amounts to 1.3 billion tons per year.<sup>2</sup> Reducing food waste is critical for combating hunger, improving food security, and reducing the environmental impact (e.g., CO<sub>2</sub> emission). Water loss, tissue metabolism, texture deterioration, and microbial growth are the factors contributing to the loss of fresh produce.<sup>3–5</sup> To decelerate spoilage, food packaging is largely used to extend shelf life, but the increase in the amount of plastic waste worldwide is a counteracting issue.<sup>6</sup> The prevailing packaging technologies, such as metalized plastic and metal oxide thin films, provide a relatively impermeable layer to oxygen but tend to have weak adhesion, poor flexibility, and poor recyclability and require costly vacuum-based processing.<sup>7,8</sup> Multilayer polymeric thin films deposited from water using polyelectrolytes have shown extraordinarily low oxygen permeability and are of high interest due to their better flexibility, microwavability, ease of fabrication, and better recyclability compared to those of their inorganic counterparts.<sup>9</sup> Due to the growing interest in environmental friendliness, biobased materials have received more attention as an alternative to synthetic polyelectrolytes. In this context, the development of greener, more cost-effective food packaging is essential to alleviating both food and plastic waste.

For food packaging, merely biodegradable or biocompatible is not enough. Edible coatings have been widely investigated to make food packaging more sustainable. Ruggeri et al. demonstrated the utility of silk fibroin and poly(vinyl alcohol) blends in creating an edible coating that significantly reduces weight loss and color change of fresh-cut apples.<sup>10</sup> Jung et al.

utilized egg-derived polymers and cellulose nanomaterials to form bionanocomposite coatings for perishable produce.<sup>11</sup> Among biobased packing materials originating from naturally renewable resources, polysaccharides such as starch, chitosan, alginate, carrageenan, pectin, and cellulose derivatives are the most notable for the preparation of edible films.<sup>12–14</sup> In general, polysaccharides have good gas barrier properties and have wide applications in the medical and food industries.<sup>15,16</sup> Multilayered thin films of chitosan and carrageenan, deposited using the layer-by-layer assembly technique, have a high gas barrier that could be used for food packaging.<sup>17</sup>

In the study presented here, a unique edible coating, with optical transparency and a high gas barrier, was prepared by coupling chitosan (CH) and pectin (PT) in a polyelectrolyte complex (PEC). Chitosan is a naturally occurring polysaccharide that has been used in numerous applications due to its biocompatibility, biodegradability, and availability.<sup>18–20</sup> Chitosan is obtained by deacetylation of chitin, which is largely found in the exoskeleton of crustaceans and fungal cell walls.<sup>21</sup> As shown in Figure 1a, chitosan is a polycation that consists of  $\beta$ -1,4-linked D-glucosamine. Pectin is a negatively charged heteropolysaccharide found in plant cell walls. The composition of pectin varies, but its primary component is  $\alpha$ -(1–4)-linked D-galacturonic acid units (Figure 1a). The amine groups in chitosan and the carboxylic acid groups in pectin form a highly ionically cross-linked network upon adjustment of the pH with a citric acid solution. A 1.5  $\mu\text{m}$  CH/PT PEC coating

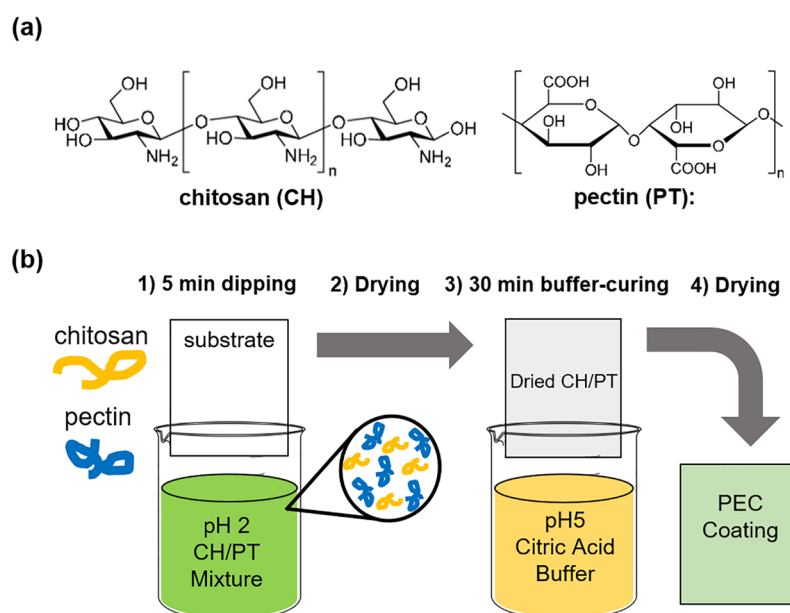
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**Figure 1.** (a) Chemical structures of chitosan (CH) and pectin (PT). (b) Schematic of the edible polyelectrolyte complex dip-coating process.

on the PET film exhibits an oxygen transmission rate of  $0.291 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$  and prevents the browning of apple slices for hours. This high-barrier edible polyelectrolyte pair demonstrates a unique opportunity for reducing food and plastic packaging waste.

## EXPERIMENTAL SECTION

**Materials.** Chitosan (item FGC-1, 95% deacetylated, 50–60 cP) was purchased from G. T. C. Union Group Ltd. (Qingdao, China). Pectin (PT, from apple, 50–75% esterification), citric acid (CA, ACS reagent), hydrochloric acid (HCl, ACS reagent, 37%), sodium hydroxide (NaOH, ACS reagent, pellets), and sodium chloride (NaCl, ACS reagent) were purchased from Sigma-Aldrich (Milwaukee, WI). All aqueous solutions were prepared in 18 M $\Omega$  deionized (DI) water, which was also used for all rinsing procedures. A poly(ethylene terephthalate) film (PET, 179  $\mu\text{m}$  thick, ST505, Dupont-Teijin) was purchased from Tekra (New Berlin, WI) and used as the substrate for oxygen transmission rate measurements.

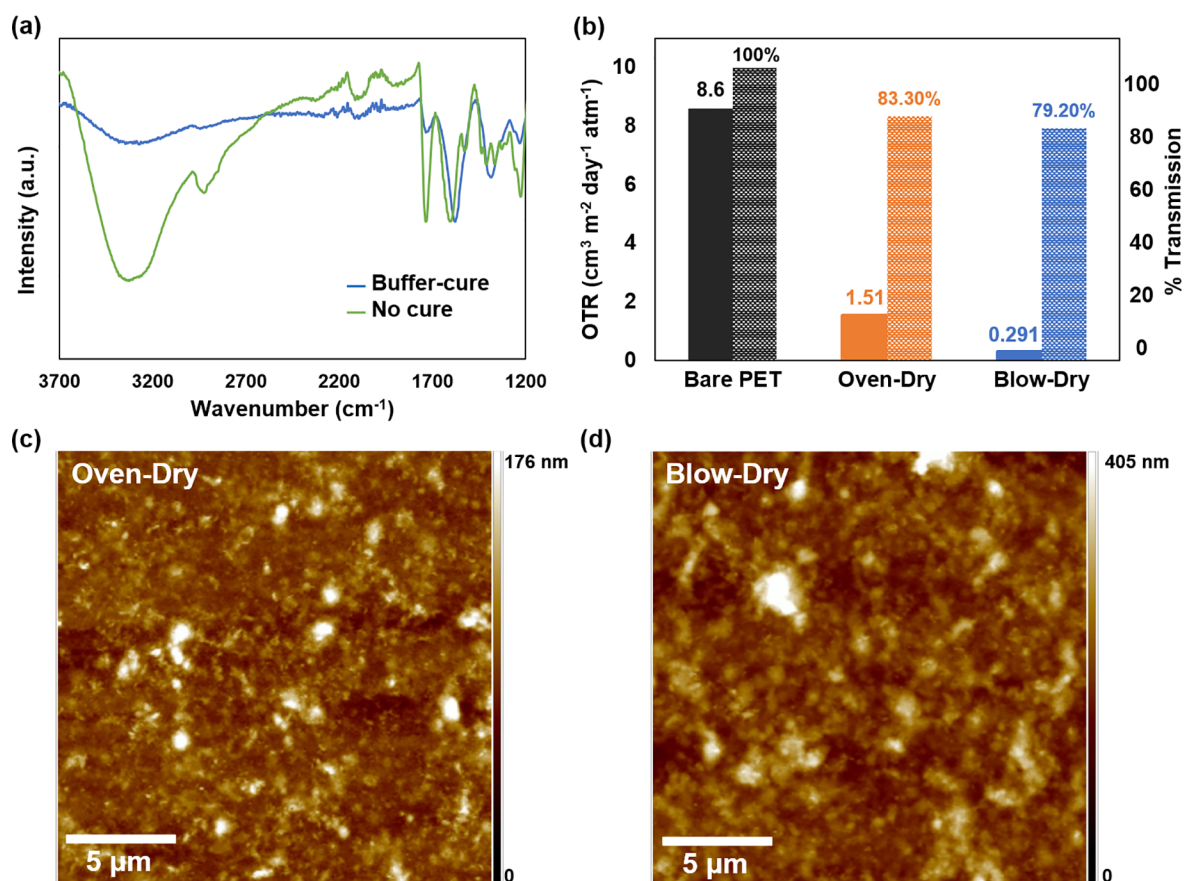
**Preparation of Edible Coating.** A 1 wt % CH solution was prepared in 18 M $\Omega$  DI water by adjusting the pH to 1.5 using 1 M HCl and stirring for 3 h. A 3 wt % PT solution was prepared in 18 M $\Omega$  DI water and rolled for at least 12 h to fully dissolve the powder. The polyelectrolyte complex (PEC) mixture was prepared by mixing equal volumes of the two solutions, rolling for at least 12 h to achieve a homogeneous solution. The final pH 2 PEC mixture (0.5 wt % CH and 1.5 wt % PT) was used for dip-coating. PET film was rinsed with methanol and DI water and dried with compressed air, followed by corona treatment immediately before coating. The coating procedure is shown in Figure 1b. Substrates were immersed in the coating solution for 5 min and then dried at 70  $^{\circ}\text{C}$  for 5 min and 150  $^{\circ}\text{C}$  for 1 h (oven dry) or dried with compressed air (blow dry). The dried films were then cured with pH 5 200 mM CA buffer for 5 min, followed by DI water rinsing and the same drying procedure. Deposition of the film on a silicon wafer (*p*-doped, single-side polished from University Wafers, Boston, MA) or Au/Ti electrode quartz crystals (Maxtek, Inc., Cypress, CA) was carried out in the same manner, except the wafer or the crystal was subjected to plasma cleaning (32G Plasma Cleaner, Harrick Plasma, Ithaca, NY) for 5 min instead of corona treatment. The coating was deposited on bananas and fresh-cut apple slices using the blow-drying method and tested under ambient conditions [ $\sim 23$   $^{\circ}\text{C}$  and 50–75% relative humidity (RH)].

**Characterization of Thin Films.** Fourier-transform infrared spectroscopy (FTIR) was used to compare the films on the silicon

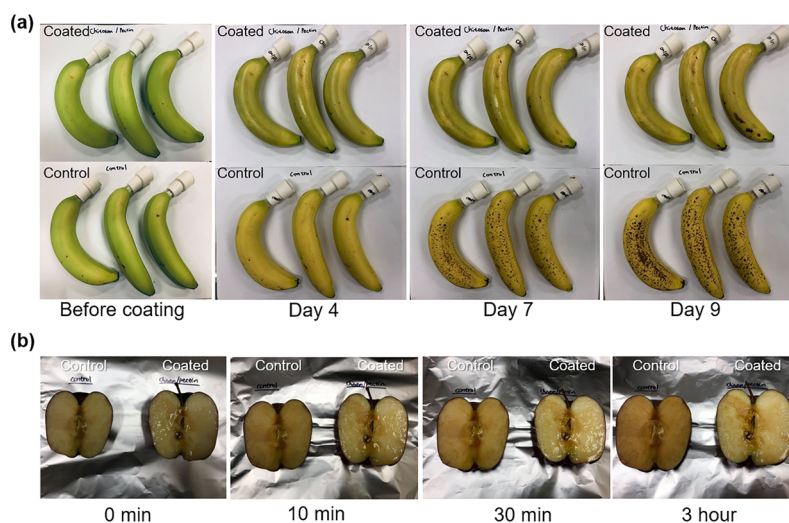
wafer before and after buffer curing using an Alpha Platinum-ATR FTIR spectrometer (Bruker, Billerica, MA). The thickness of thin films was measured on a quartz crystal using a P6 profilometer (KLA-Tencor, Milpitas, CA). The coating weight was measured with a Maxtek Research Quartz Crystal Microbalance (RQCM) (Infinicon, East Syracuse, NY), with a frequency range of 3.8–6 MHz, in conjunction with 5 MHz quartz crystals. The film density was calculated using the thickness and weight data. The film surface morphology on a silicon wafer was characterized using a Dimension Icon atomic force microscope (AFM, Bruker) in tapping mode. The transmittance of light through a coating deposited on PET was measured at 550 nm using a USB2000 ultraviolet–visible (UV–vis) spectrometer (Ocean Optics, Dunedin, FL). Light transmission was normalized by making uncoated PET 100% transmission. The oxygen transmission rate (OTR) was tested by AMETEK MOCON Inc. (Minneapolis, MN), using an Oxtran 2/21 ML instrument at 23  $^{\circ}\text{C}$  under 0% RH, in compliance with ASTM D3985. The repeatability associated with the OTR analyzer is 0.002 or 1%, whichever is greater.

## RESULTS AND DISCUSSION

The structure of a polyelectrolyte complex relies on the interactions between polycation and polyanion components,<sup>22,23</sup> whose many interfaces reduce the oxygen permeability.<sup>24</sup> The  $\text{pK}_a$  of the amine group on chitosan is  $\sim 6.5$ ,<sup>25</sup> while that of pectin is 2.8–4.1, so the galacturonic acid unit is negatively charged at pH values above this range.<sup>26</sup> When the chitosan and pectin solutions are mixed at pH 2, a homogeneous solution is formed without strong ionic interactions between the two biopolymers. To deposit oppositely charged polyelectrolytes simultaneously, the inhibition of electrostatic interaction is needed to prevent complexation in the solution. The CH/PT mixture can be deposited on various substrates by immersion for 5 min, likely adhering via van der Waals forces and dipole interactions.<sup>27</sup> After deposition, the coating is dried to eliminate excess water, which immobilizes the CH/PT complex. Strong ionic interaction (or complexation) is triggered by increasing the pH via buffer curing (i.e., exposure to a pH 5 citric acid buffer solution), where the carboxylic acid groups of pectin are deprotonated (i.e., become negatively charged) and the amino groups of chitosan remain protonated (positively charged).



**Figure 2.** (a) FTIR spectra of the CH/PT film before and after buffer curing. These spectra have been overlaid with an arbitrary offset for the sake of clarity. The suppressed N–H/O–H stretch ( $\sim 3200$  cm<sup>-1</sup>) indicates ionic cross-linking with buffer curing. (b) Oxygen transmission rate (right axis) of uncoated and coated 179 μm PET, measured at 23 °C and 0% RH. Normalized light transmission of films measured at 550 nm (left axis). Atomic force micrograph of (c) oven-dried and (d) blow-dried CH/PT film deposited on a silicon wafer.



**Figure 3.** (a) Comparison of CH/PT-coated and uncoated banana ripening as a function of time. Bananas were aged under ambient conditions. (b) Comparison of CH/PT-coated and uncoated apple browning as a function of time under ambient conditions.

This highly ionically cross-linked structure imparts a high gas barrier due to the small free volume and high cohesion energy within the PEC.<sup>28,29</sup> FTIR spectroscopy was used to examine the buffer curing of the CH/PT coating. The N–H/O–H stretch ( $\sim 3200$  cm<sup>-1</sup>) is suppressed after curing, indicating

that ionic cross-linking has occurred (Figure 2a). A substantial decrease in the relative intensity of the COOH carbonyl stretch at 1736 cm<sup>-1</sup> is also observed. This further suggests that a majority of the carboxylate groups are deprotonated following buffer immersion.

The oven-dry method for the edible PEC consumes energy, but the coating can also be dried with blowing compressed air. The postprocessing also influences the film thickness.<sup>30</sup> Once the coating is dry, this dip-coating process results in a transparent, highly conformal thin film, with an average thickness of  $574 \pm 27$  nm (oven dry) or  $1.480 \pm 0.057$   $\mu\text{m}$  (blow dry). The QCM reveals the coat weight of the edible coating is  $76.85 \pm 0.51$   $\mu\text{g}/\text{cm}^2$  (oven dry) or  $179.75 \pm 0.10$   $\mu\text{g}/\text{cm}^2$  (blow dry). The density of the oven-dried film is  $1.23 \pm 0.05$   $\text{g}/\text{cm}^3$ , while the density of the blow-dried film is  $1.21 \pm 0.04$   $\text{g}/\text{cm}^3$ . Density is independent of the method of drying, suggesting the structure of CH/PT coatings is very similar. The thinner coating of the oven-dried film is likely due to the influence of temperature that affects the viscosity of the CH/PT mixture. At higher temperatures, the solution has reduced viscosity, which results in a lower coat weight.

Oxygen barrier testing was performed at 23 °C under 0% RH. The oxygen transmission rate (OTR) values of the oven-dried and blow-dried films deposited on 179  $\mu\text{m}$  PET are 1.51 and 0.291  $\text{cm}^3 \text{m}^{-2} \text{day}^{-1} \text{atm}^{-1}$ , respectively (Figure 2b). The oven-dried and blow-dried CH/PT films reduce the OTR of the PET by almost 6 and 30 times, respectively. The gas barrier is dependent on thickness, which accounts for the difference between the drying methods. The transmission of light through these coatings was measured by UV–vis spectrometry at 550 nm and normalized with uncoated PET. The oven-dried film transmits 83.3% of light, while the blow-dried film has 79.2% light transmission. This difference in light transmission can be explained by the difference in the film thickness and surface roughness. The morphology and surface roughness of CH/PT PEC films were measured using an AFM. Panels c and d of Figure 2 show the topography of these coatings deposited on a silicon wafer. The oven-dried film has a smoother surface, with an  $R_q$  of 16 nm, while the blow-dried film has a rougher surface, with an  $R_q$  of 40 nm.

When this edible PEC coating is deposited on bananas (Figure 3a), slower ripening is observed relative to that of uncoated fruit, which was dipped in DI water solutions adjusted to the same pH as the CH/PT PEC solution. The coated bananas remain green after 1 week, while the uncoated bananas already exhibit brown speckles associated with spoilage. The PEC was also applied to apple slices (Figure 3b), which were dipped into solutions immediately after being cut. The uncoated apple slice browned within 10 min, but the edible CH/PT coating prevented browning for up to 3 h. This blow-dried CH/PT PEC coating has a very high oxygen barrier, with an OTR of 0.291  $\text{cm}^3 \text{m}^{-2} \text{day}^{-1} \text{atm}^{-1}$  and an oxygen permeability of  $1.02 \times 10^{-18}$   $\text{cm}^3 \text{cm cm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ , which is why it can effectively prevent spoilage and provides extended shelf life.

In summary, a protective coating for fruit was prepared from a polyelectrolyte complex of chitosan as polycation and pectin as polyanion. This edible coating was deposited via dip-coating, followed by oven or blow drying and buffer curing with a citric acid solution. The blow-dried film imparts a low OTR of 0.291  $\text{cm}^3 \text{m}^{-2} \text{day}^{-1} \text{atm}^{-1}$ , while retaining 79.2% light transmission, with a thickness of only 1.5  $\mu\text{m}$ . With an oxygen permeability of  $1.02 \times 10^{-18}$   $\text{cm}^3 \text{cm cm}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ , this is one of the best barriers ever reported using only generally recognized-as-safe (GRAS) polymers. When deposited on perishable fruits, this imperceptible protective layer slows the ripening of bananas and browning of apple slices. These results suggest that an edible CH/PT PEC coating

could be useful for extending the shelf life of perishable produce, reducing food and plastic packaging waste.

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### Notes

The authors declare no competing financial interest.

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