Enhancing the properties of fish gelatin edible film by proanthocyanidin-titanium coordination crosslinking effect

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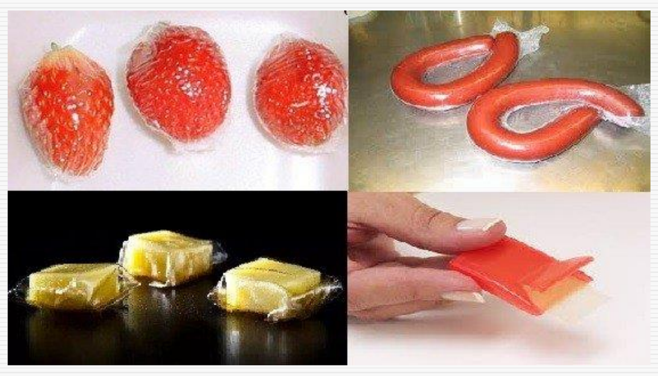
Introduction

Edible film, a potential candidate to replace the plastic package, has been discovered for quite a long time. But some poor properties, especially poor mechanical properties, need to be improved before expending applications of the edible films.

Background and Motivations

- **Proanthocyanidin**
  - **Rich in vegetables and fruits**
  - **Provide astringency mouth feel**
  - **Has antioxidant ability**

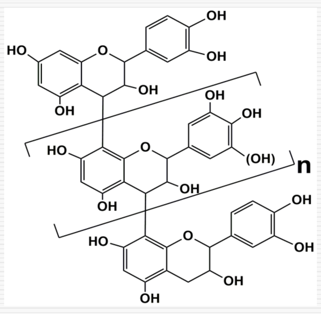
- **Edible film**
  - **Edible food package**
  - **Protection**
  - **Environmental friendly**



Proanthocyanidin (PA), also known as condensed tannin, is widely distributed in fruit and vegetables. Researchers have discovered the PAs or titanium can be individually applied as edible film crosslinkers. In fact, the PAs are also found highly reactive to metal ions (such as Fe^{3+}) and able to aggregate and form polymer networks through chelating bonds[4]. But how about the PA-Ti^{4+} chelating reaction? Can it provide coordination crosslinking effects and further improve the properties of edible films?

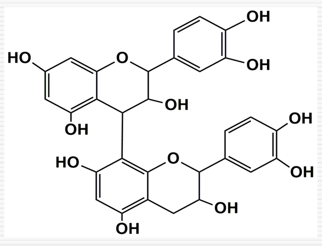
Methods

Proanthocyanidin polymer



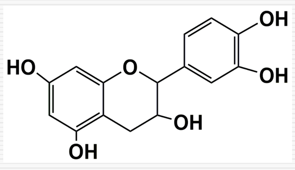
Hop tannin
Mn = 3581 Da

Proanthocyanidin Dimer



Procyanidin B2
Mw = 578 Da

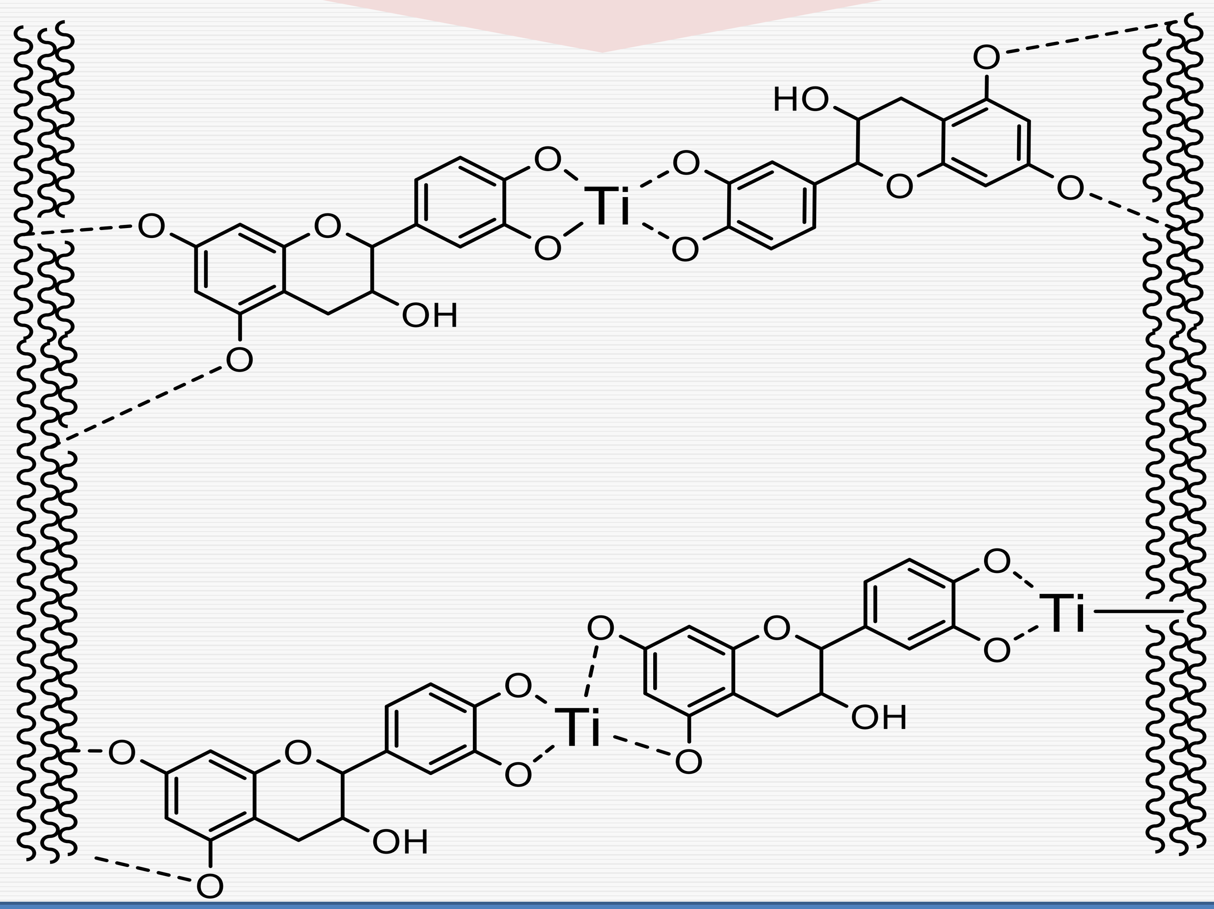
Proanthocyanidin monomer



Catechin
Mw = 290 Da

Titanium (Ti^{4+})

Coordination crosslink effect through proanthocyanidin-Ti^{4+}chelating reaction

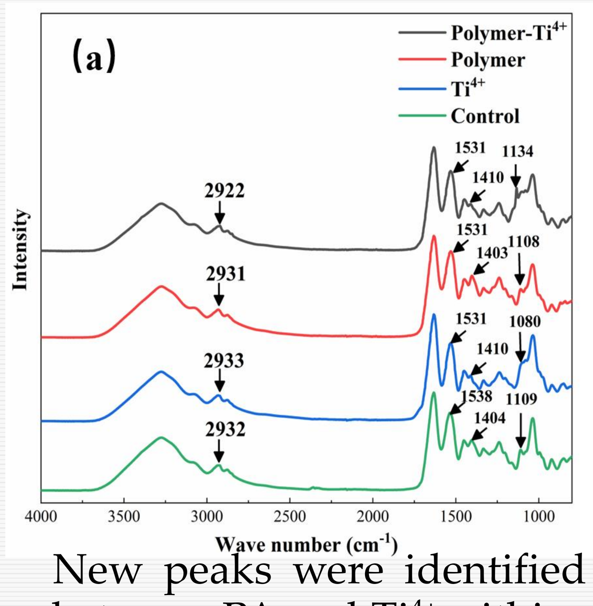


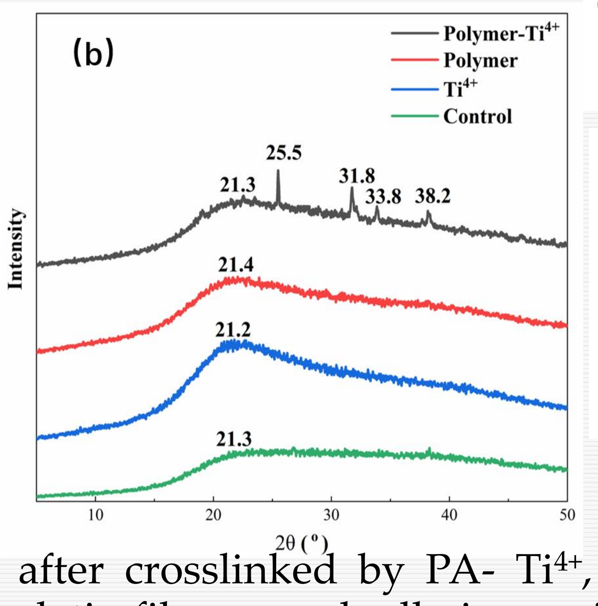
Results and Discussions

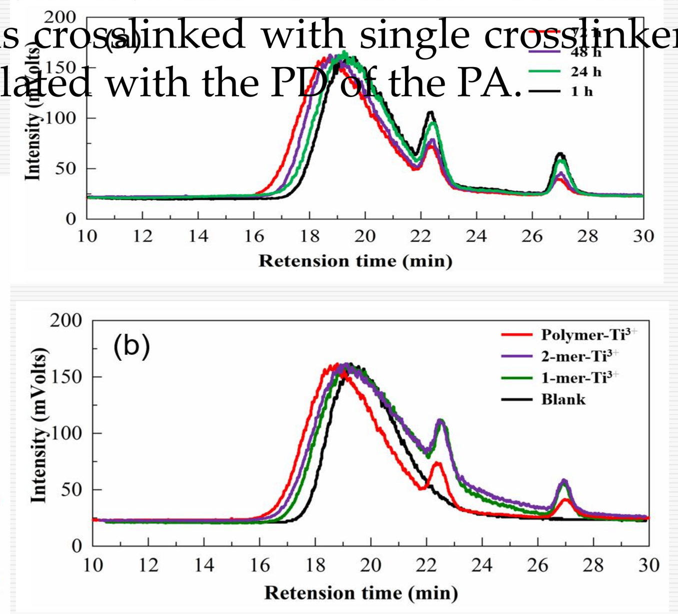
Table 1 the mechanical properties of the gelatin films

Crosslinker	Thickness	TS (MPa)	EAB (%)
PA polymer-Ti^{4+}	0.29 ± 0.03	7.51 ± 0.93	31.27 ± 1.25
PA polymer	0.31 ± 0.04	6.35 ± 0.82	21.33 ± 0.44
PA dimer- Ti^{4+}	0.36 ± 0.04	2.43 ± 0.28	30.12 ± 2.96
PA dimer	0.30 ± 0.03	1.71 ± 0.11	24.12 ± 3.15
PA monomer-Ti^{4+}	0.30 ± 0.04	1.73 ± 0.15	28.11 ± 1.33
PA monomer	0.31 ± 0.03	1.35 ± 0.14	20.43 ± 3.11
Ti^{4+}	0.36 ± 0.02	1.11 ± 0.77	21.42 ± 4.33
None	0.27 ± 0.04	0.09 ± 0.02	10.33 ± 1.27

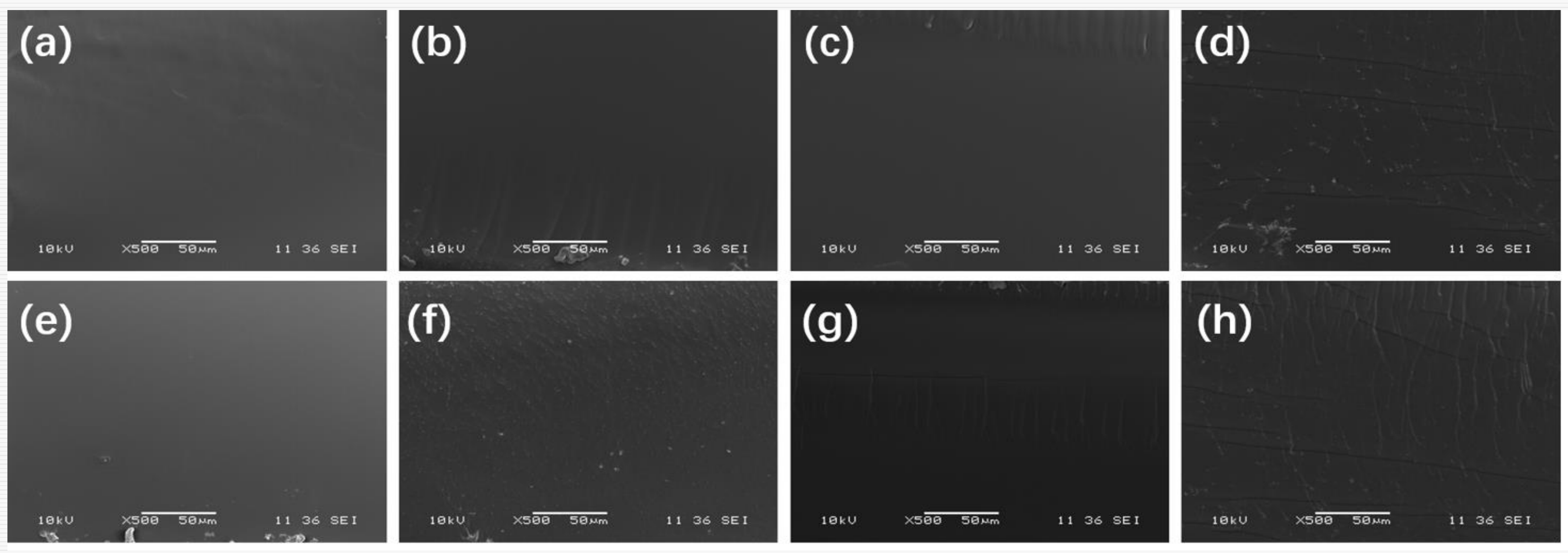
Crosslinked films showed higher TS and EAB than film without crosslink treatments. The films crosslinked by PA-Ti4+ showed higher TS and EAB than the films crosslinked with single crosslinker (PA or Ti4+). TS of PA-Ti4+ crosslinked films showed positively related with the PD of the PA.







New peaks were identified after crosslinked by PA- Ti^{4+}, represent the chelating reaction between PA and Ti^{4+} within gelatin film. a gradually increasing gelatin molecular weight after crosslinking treatment. Furthermore, the molecular weight of the gelatin was also affected by the type of the crosslinker, the higher the PD of the PA, the higher the gelatin molecular weight were observed.



The gelatin film basically showed relatively smooth surface morphology (Figure 3), but their surface showed different hydrophobicity after crosslink treatments (Table 2). As for the film crosslinked by PA-Ti4+, the surface showed higher contact angles, indicated more hydrophobic surfaces. But for the films without crosslinked by Ti4+, lower contact angles were observed. Films crosslinked by PA and PA-Ti4+ presented DPPH scavenging abilities. But for the films crosslinked by Ti4+ or without crosslinking treatment, poor DPPH scavenging abilities were shown

Table 2 Particle size, contact angle and DPPH scavenging ability

Crosslinker	Average size (nm)	Contact angle (°)	DPPH scavenging (%)
Polymer-Ti^{4+}	447.2 ± 18.32	119.9 ± 10.9	72.3 ± 1.26
Polymer	16.42 ± 1.04	53.1 ± 1.6	92.5 ± 3.11
Dimer- Ti^{4+}	17.33 ± 3.11	130.3 ± 1.4	61.3 ± 1.82
Dimer	7.66 ± 1.21	53.2 ± 1.7	92.4 ± 1.66
Monomer-Ti^{4+}	16.83 ± 1.44	111.0 ± 3.9	85.4 ± 3.11
Monomer	7.42 ± 0.73	58.1 ± 4.2	90.1 ± 4.33
Ti^{4+}	14.66 ± 1.32	107.3 ± 5.6	0
None	5.15 ± 0.26	39.4 ± 3.2	0

Conclusions

PA and Ti^{4+} were applied to crosslink fish skin gelatin based edible films, the coordination crosslink effects were observed on the aspect of mechanical properties, gelatin particle size and molecular weight. The bigger the PD of the PA, the better the coordination effect were observed. Furthermore, the films provided fine surface morphology and hydrophobicity and antioxidant activity. These results not only in agree with the phenomenon observed in leather industry, which applied the PA-metal ion chelating to improve the quality of leather, it also implied other polyphenols (such as hydrolysable tannin) and non-toxic metal ions could also have this coordination effect on edible film crosslinking.

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