UV-Shielding and Clusteroluminogenic Cellulose-Based Films with Tuneable Wettability and Permeability for Dually Self-Indicating Food Packaging

Wing-Fu Lai,Wan Yip,Wing-Tak Wong

Abstract

Food packaging plays a vital role not only in extending the shelf-life and ensuring the safety and quality of food, but also in reducing the occurrence of food loss and waste. This study reports the generation of biocompatible and tuneable cellulose-based films, which show strong UV absorbing capacity in both UVA and UVB regions to protect the packaged food from UV degradation. By taking advantage of the process of clusterization-triggered emission, the films can indicate, by displaying changes in the intensity of luminescence, not only their properties but also the status of the packaged food. The protective and dually self-indicating capacity of the films in food packaging is demonstrated by using frozen chicken breast as a food model. Together with their negligible toxicity, good barrier properties, and high tunability, the films warrant further development as dually self-indicating materials for food packaging applications.

1 Introduction

Food packaging aims at protecting food products from environmental contamination or influences from various factors, ranging from microorganisms and humidity to light and odor.[1] It, therefore, plays a vital role not only in extending the shelf-life and ensuring the safety and quality of food, but also in reducing the occurrence of food loss and waste. Over the years, different types of films have been developed and characterized for food packaging. One example is the chitosan-gelatin biocomposite films incorporated with the quercetin-starch complex.[2] It can protect food products via its antibacterial, antioxidative, and barrier properties.[2] Another example is the polyvinyl alcohol (PVA)/starch film loaded with anthocyanin and propolis extract.[3] The film has been demonstrated to protect dairy products from spoilage.[3] Recently, cellulose acetate films incorporated with various carotenoids (including lycopene, norbixin, and zeaxanthin) have been examined for active food packaging.[4] The one containing norbixin has successfully preserved the activity of vitamin B2 stored under a photooxidative environment.[4] Similar success in food preservation has been achieved by Hashmi and co-workers,[5] who have generated electrospun composite nanofiber mats by using carboxymethyl cellulose and have effectively preserved the freshness of stored fruits and vegetables. All these have demonstrated the versatility and diversity of films developed for food applications.

To enhance the functionality of packaging films and to increase the efficiency in food protection, various luminescent films have recently been exploited for use in food packaging. Fabrication of these films, however, necessitates the addition of luminogens (such as metal oxide nanoparticles,[6] ruthenium tris-1,10-phenanthroline,[7] and fullerene C70[7]). Release of these luminogens into the packaged food may not only affect the sensory properties of the food, but may also raise safety concerns. To address this problem, this study reports nonconjugated luminescent polymeric films generated from a clusteroluminogenic polymer, which is designated as CT and has previously been examined in a preclinical trial for self-illuminating therapy.[8] Contrary to existing

luminescent food packaging films, the emissive properties of our films come from the intrinsic luminescence of CT. This ameliorates the problem caused by the addition and release of potentially toxic luminogens. By taking advantage of the fact that the intensity of clusterization-triggered emission (CTE) is influenced by the molecular entanglement of polymeric molecules,[9] our films reveal, via an alteration in the intensity of intrinsic luminescence, changes in not only their properties but also the status of the packaged food. Along with their high tunability, negligible toxicity, UV-shielding capacity, and good barrier properties, our films show the potential to mediate comprehensive and dually self-indicating packaging during food storage and protection.

2 Results and Discussions

2.1 Film Preparation and Structural Evaluation

The use of cellulose has been extensively exploited in food packaging research not only because of its natural origin and good mechanical strength,[10] but also due to its track record of applications as food additives, particularly as food fillers and stabilizers to enhance the stability and sensory properties of food matrices.[11] The polymer, namely CT, adopted in this study is a cellulose-based derivative previously developed for bioactive agent delivery (**Figure 1A**).[8, 12] Its synthesis starts from hydroxypropylation and methylation of cellulose, followed by transesterification which is facilitated by the use of a polar aprotic solvent as the reaction medium.[8] CT shows film-forming capacity, and can generate films with macroscopic homogeneity (Figure **1B**). In this study, cellulose modified by hydroxypropylation (degree of substitution = 7–12%) and methylation (degree of substitution = 28–30%) is designated as CE. CE06, CE15, and CE50 designate CE whose 2% aqueous solution at ambient conditions has the viscosity of 6, 15, and 50 mPa·s, respectively. CT generated from CE06, CE15, and CE50 is designated as CT06, CT15, and CT50, respectively.

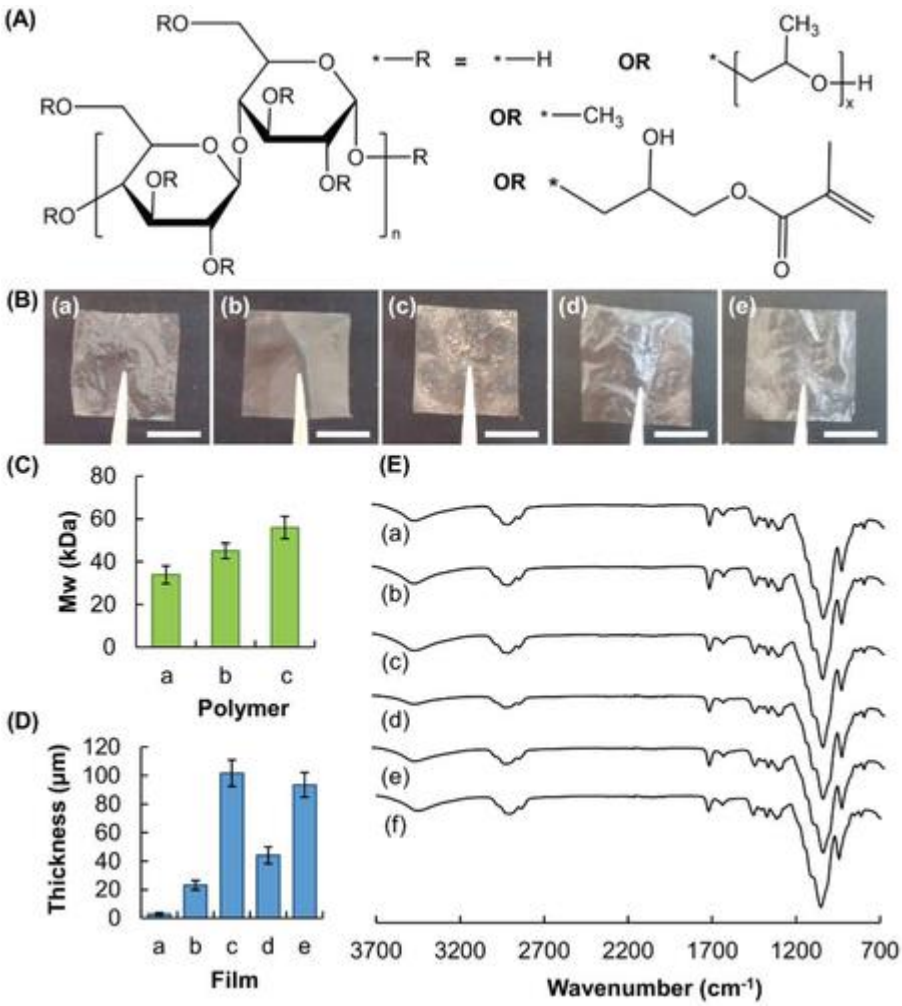

Figure 1 A) Chemical structure of CT. B) Photos of (a) F0601, (b) F0605, (c) F0610, (d) F1505, and (e) F5005. Scale bar = 1 cm. C) Weight-average molecular weights of (a) CT06, (b) CT15, and (c) CT50. D) Thickness of (a) F0601, (b) F0605, (c) F0610, (d) F1505, and (e) F5005. E) FT-IR spectra of (a) CT06, (b) CT15, (c) CT50, (d) F0605, (e) F1505, and (f) F5005.

The weight-average molecular weights of CT06, CT15, and CT50 are estimated by gel permeation chromatography (GPC) to be around 33.9, 45.1, and 55.9 kDa, respectively (Figure **1C**). The thickness of the film, prepared with the same amount of the film-forming solution, increases from 2.9 ± 0.9 to 101.7 ± 9.3 μm when the concentration of CT increases from 1% w/v to 10% w/v, and from 23.0 ± 3.3 to 93.5 ± 8.6 μm when the weight-average molecular weight of CT increases from 33.9 to 55.9 kDa (Figure **1D**). The change in film thickness is partially attributed to the change in the viscosity, and hence spreadability, of the film-forming solution when the concentration or molecular weight of CT is altered. As demonstrated by our previous study,[8] the higher the concentration or molecular weight of CT, the higher the viscosity of the CT solution. This leads to a decline in the spreadability of the solution during film production and hence an increase in film thickness. To determine the structure of CT, Fourier-transform infrared (FT-IR) spectroscopy is applied (Figure **1E**). In the spectra of CT06, CT15, and CT50, a broad peak

is observed at around 3440 cm^{-1}. It is contributed by the stretching vibrations of OH groups in the cellulose backbone. Signals at 1051 and 1385 cm^{-1} represent the stretching vibrations of C O bonds and the bending vibrations of OH groups, respectively. The peak at 1720 cm^{-1} is assigned to C O stretching vibrations of methacrylate groups. Meanwhile, signals are detected in the wavenumber range between 2800 and 3000 cm^{-1}. These signals are attributed to C H stretching vibrations of CT. No apparent change in the spectra of CT before and after film preparation is observed. This reveals that the process of film formation causes no significant change in the structure of CT.

2.2 Properties of the Films for Food Packaging

The mechanical strength of a film is a factor determining the performance in food packaging. By changing the CT concentration of the film-forming solution from 1% to 10% w/v or by increasing the molecular weight of CT, the extent of molecular entanglement experienced by CT molecules is enhanced, leading to an increase in the maximum tensile strength and elongation at breakage (**Figure 2A**). The thermal stability of different film samples is examined by using thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) (Figure **2B**,**C**). The TGA and DTG curves suggest that the films, regardless of the concentration or molecular weight of CT adopted, are thermally stable up to the temperature of around 300 °C, after which thermal decomposition occurs, resulting in a significant reduction in the weight percentage at around 300–400 °C (Δ_m = 80.98%).

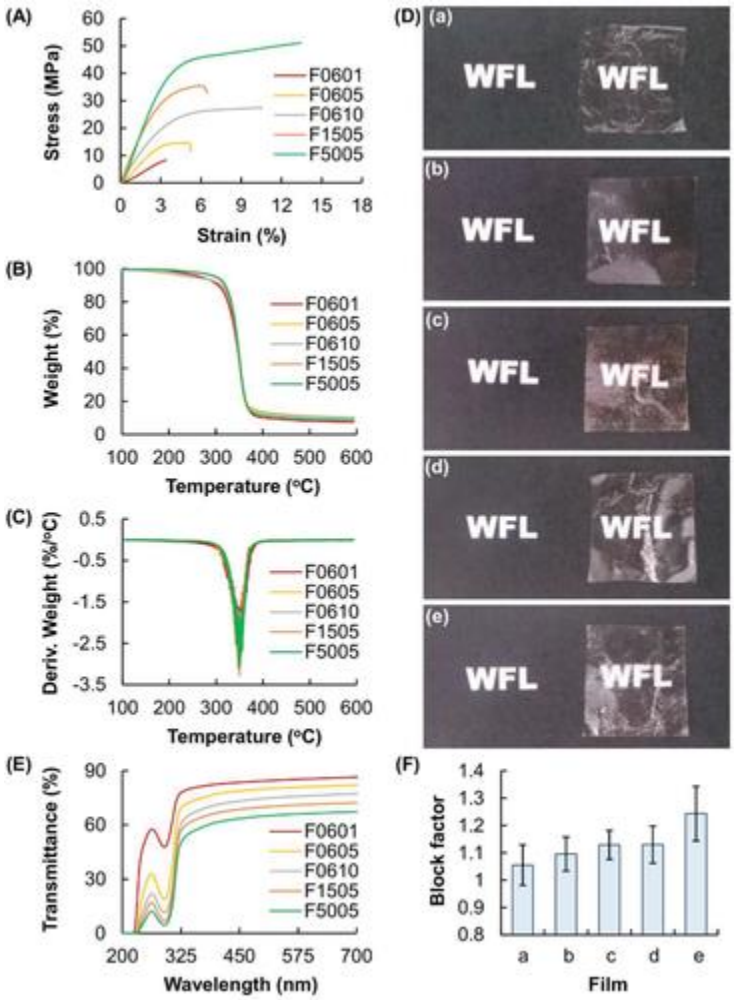

Figure 2 A) Stress–strain curves, B) TGA curves, and C) DTG curves of different films. D) Photos of different films [(a) F0601, (b) F0605, (c) F0610, (d) F1505, and (e) F5005] placed over printed text to demonstrate the high transparency of the films. E) UV–vis transmittance spectra and F) UV block factors of different films: (a) F0601, (b) F0605, (c) F0610, (d) F1505, and (e) F5005.

Apart from the mechanical strength and thermal stability, the opacity of a film has to be considered as it is an important parameter for film appearance which can influence the degree of consumer acceptance. The UV–vis spectra reveal that all films are optically transparent with transmittance of around 60–85% in the visible range (400–700 nm) (Figure 2D,E). An increase in the concentration or molecular weight of CT leads to a reduction in transmittance. All films show UV-absorbing capacity in both UVA (320–400 nm, long-wavelength radiation) and UVB (280–320 nm, short-wavelength radiation) regions, with the UV block factor lying between 1.05 and 1.24 (Figure 2F). Our films can, therefore, avoid UV degradation of the packaged food by remarkably reducing UV transmission.

In order to be used as a direct food contact material for food packaging, the films need to be nontoxic. In this study, the toxicity of the films is evaluated both in vitro and in vivo. In

the former, HepG2 cells are adopted because of their unlimited availability, phenotypic stability, and importantly, genotypic features typical of normal liver cells.[13, 14] They have been regarded as an alternative to primary human hepatocytes for cytotoxicity studies, and have been used to determine the toxicity of food packaging films.[13] On the other hand, HEK293 cells are commonly used in toxicology studies,[15] particularly in evaluating the effect of a drug candidate on the renal system.[16] The low toxicity of CT films is demonstrated by the fact that the loss of cell viability after 5 h treatment with the films is negligible in all concentrations tested (**Figure 3A**). To determine chronic toxicity in vitro, the viability of the treated cells is examined after 24 h post-treatment incubation. No detectable loss of cell viability is noted. In the in vivo context, the solution of CT leads to no significant weight loss in mice (Figure **3B**). This corroborates the negligible toxicity of the films.

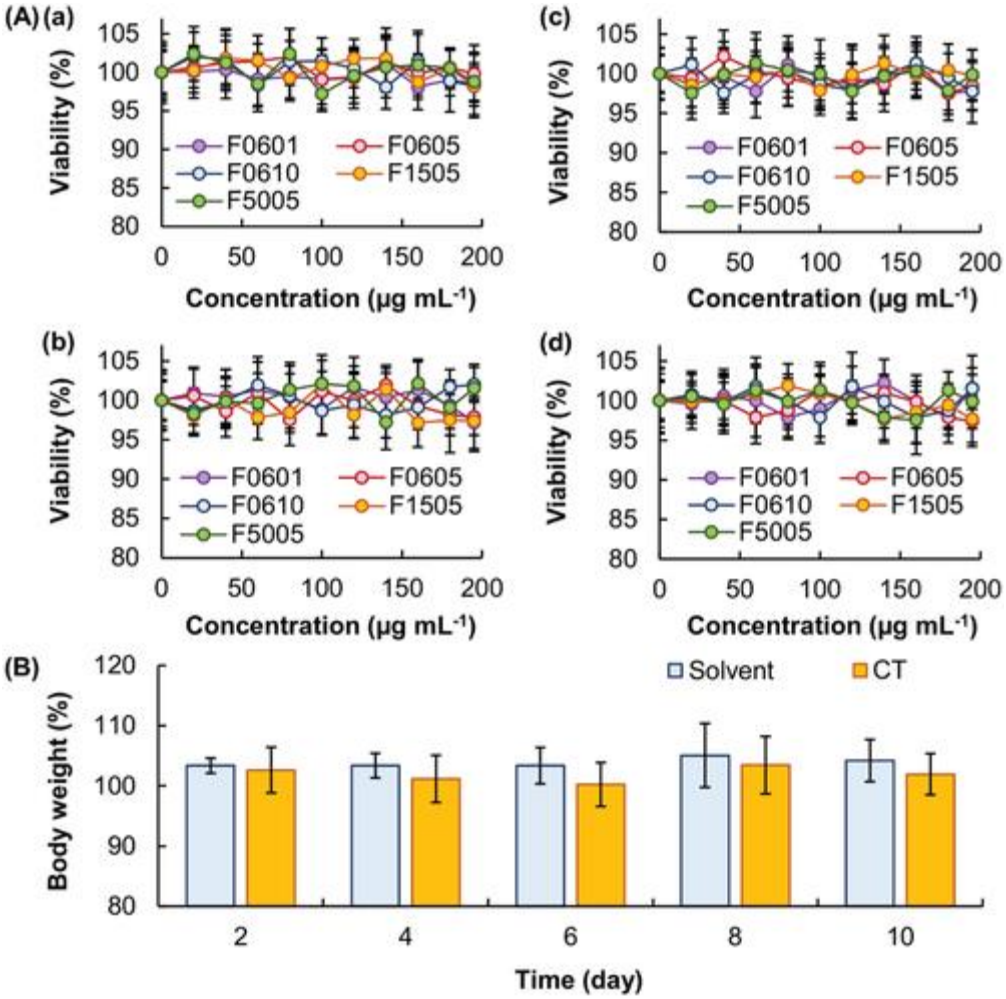

Figure 3 A) Viability of (a,b) HepG2 and (c,d) HEK293 cells after 5 h treatment with different films, (a,c) before and (b,d) after subsequent 24 h post-treatment incubation. B) Changes in the relative body weight of mice injected intraperitoneally with a CT solution. The solvent is used as a control.

2.3 Performance of the Films in Serving as Barriers

Scanning electron microscopy (SEM) analysis of the cross-section of the films shows that, regardless of the concentration or molecular weight of CT adopted, all films have a highly compact microstructure with a low degree of porosity (**Figure 4A**). The swelling capacity and wettability are two factors affecting the water resistance property of a film.[17] The wettability of the films is determined by contact angle measurements, which demonstrate that by increasing the concentration or molecular weight of CT, the wettability of the films decrease (Figure **4B**). This is partially attributed to the increase in the hydrophobicity of CT when the molecular weight of CT increases. Meanwhile, when the concentration of the film-forming solution increases, a higher molecular entanglement density results. This leads to stronger interactions among CT molecules. Due to the competitive binding effect,[18] interactions between the hydrophilic groups of CT and water molecules are reduced, leading to lower wettability of the films. Such changes in wettability may partially explain the decrease in the equilibrium water content (EWC) of the films when the concentration or molecular weight of CT increases (Figure **4C**).

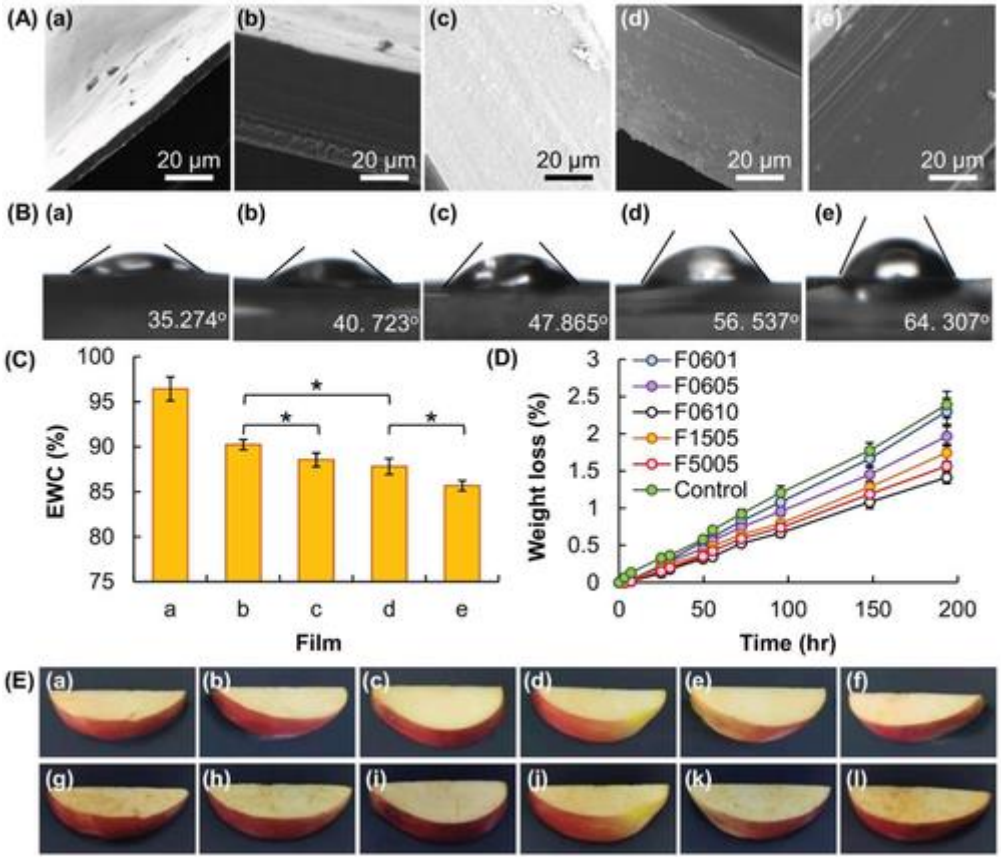

Figure 4 A) SEM micrographs of (a) F0601, (b) F0605, (c) F0610, (d) F1505, and (e) F5005. B) Water contact angles on different films: (a) F0601, (b) F0605, (c) F0610, (d) F1505, and (e) F5005. C) The equilibrium water content of different films: (a) F0601, (b) F0605, (c) F0610, (d) F1505, and (e) F5005. * denotes $p < 0.05$. D) Changes in the weight of apple pieces stored in a tube, with the hole in the cap protected by different films at 4 °C. The setup in which the hole in the cap is uncovered is used as the control. E) Photos of apple pieces stored in a tube, with the hole in the cap either protected by different films

[(a,g) F0601, (b,h) F0605, (c,i) F0610, (d,j) F1505, (e,k) F5005], or (f,l) uncovered, at 4 °C for (a–f) 0 d, and (g–l) 7 d.

To demonstrate the ability of the films to protect food from moisture loss, apple pieces are used as a food model. The extent of moisture loss is most significant in the control, in which the drilled hole in the cap is uncovered (Figure **4D**). This is consistent with the observation that the apple piece in the control shows significant signs of dehydration and enzymatic browning (Figure **4E**), which is a consequence of the oxidation reaction mediated by polyphenol oxidase (PPO) and peroxidase (POD).[19] Compared to the control, the apple pieces protected by the films show a lower degree of enzymatic browning, with less buckles and wrinkles observed. The extent of enzymatic browning and the degree of surface wrinkling reduce not only in the order of F0601 > F0605 > F0610 but also in the order of F0605 > F1505 > F5005. This suggests that the films show different barrier properties towards water vapor and oxygen, with the efficiency being positively related to the concentration and molecular weight of CT adopted. Here it is worth highlighting that while the capacity of a film in serving as a barrier to water vapor can help extend and maintain the shelf-life of the packaged food, if the water vapor permeability of the film is too low, moisture may accumulate inside the package due to various reasons (including the drip of tissue fluid from cut meats, the respiration of fresh produce, or the fluctuation in temperature in a food package with high equilibrium relative humidity).[20] This promotes mould and bacterial growth inside the package, leading to the loss of food quality. Proper control of the wettability and permeability of a packaging film is, therefore, essential for effective food protection. The high tunability of our films meets this need by enabling the barrier properties of the food package to be optimized to meet specific needs of different food products.

2.4 Applications as Dually Self-Indicating Food Packaging Films

All CT films show different degrees of luminescence under UV irradiation (**Figure 5A**), with the peak of photoluminescence (PL) and that of PL excitation (PLE) being at around 450 and 370 nm, respectively (Figure **5B**). Such luminescence is attributed to CTE,[8] during which through-space nonbonding interactions among electron-rich heteroatoms narrow down the energy gap between the HOMO and LUMO to render CT luminescent despite the absence of the conjugated structure. The concentration and molecular weight of CT adopted not only are positively related to the luminescence intensity of the films but also determine the film wettability and permeability (Figure **5C**). The concentration- and molecular weight-dependent change in the intensity of film luminescence, therefore, enables the films to be self-indicative of the barrier properties.

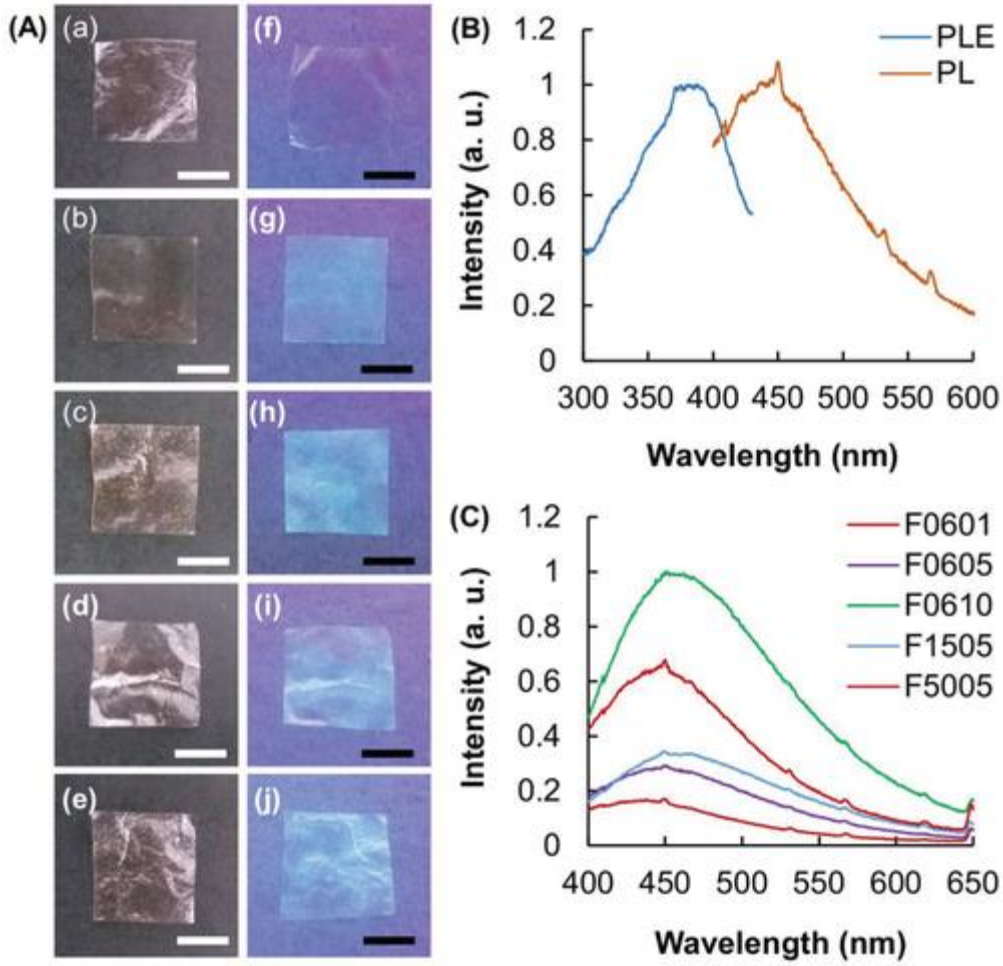

Figure 5 A) Photos of (a,f) F0601, (b,g) F0605, (c,h) F0610, (d,i) F1505, and (e,j) F5005, under (a–e) white light and (f–j) UV light. Scale bar = 1 cm. B) PL and PLE spectra of F0605. C) PL spectra of different films.

The intensity of CTE is also remarkably reduced when the films are swollen because the process of swelling leads to a lower degree of molecular entanglement (**Figure 6A**,**B**). Along with their concentration- and molecular weight-dependent luminescence intensity as mentioned above, our films display dually self-indicating capacity. To exploit the use of this capacity in food packaging, chicken breast is adopted as a food model, whose eating quality is susceptible to recurrent freeze–thaw cycles during food storage and transportation. The effect of freeze–thaw cycles on the eating quality of food products, especially meat products, has been shown by an earlier study, which reports that repeated cycles of freezing and thawing lead to changes in beef color as well as a decline in the tenderness and juiciness of the beef.[21] A similar observation has been made by Benjakul and Bauer,[22] who have found that repeated freeze–thaw cycles can damage the cells in catfish fillets to lead to a decline in sensory quality. As shown in Figure **6C**, the intensity of luminescence of the CT packaging bag is maintained when fresh chicken meat or frozen chicken meat is put inside; however, when frozen chicken meat thaws, the exudate released causes swelling of the bag, leading to a decline in the intensity of CTE. Such a change in the luminescence intensity can serve as an indicator to show the thawing of the frozen food.

Furthermore, the packaging bag effectively protects the meat from water loss (Figure 6D,E), enabling the bag to be used as a dually self-indicating device for food protection.

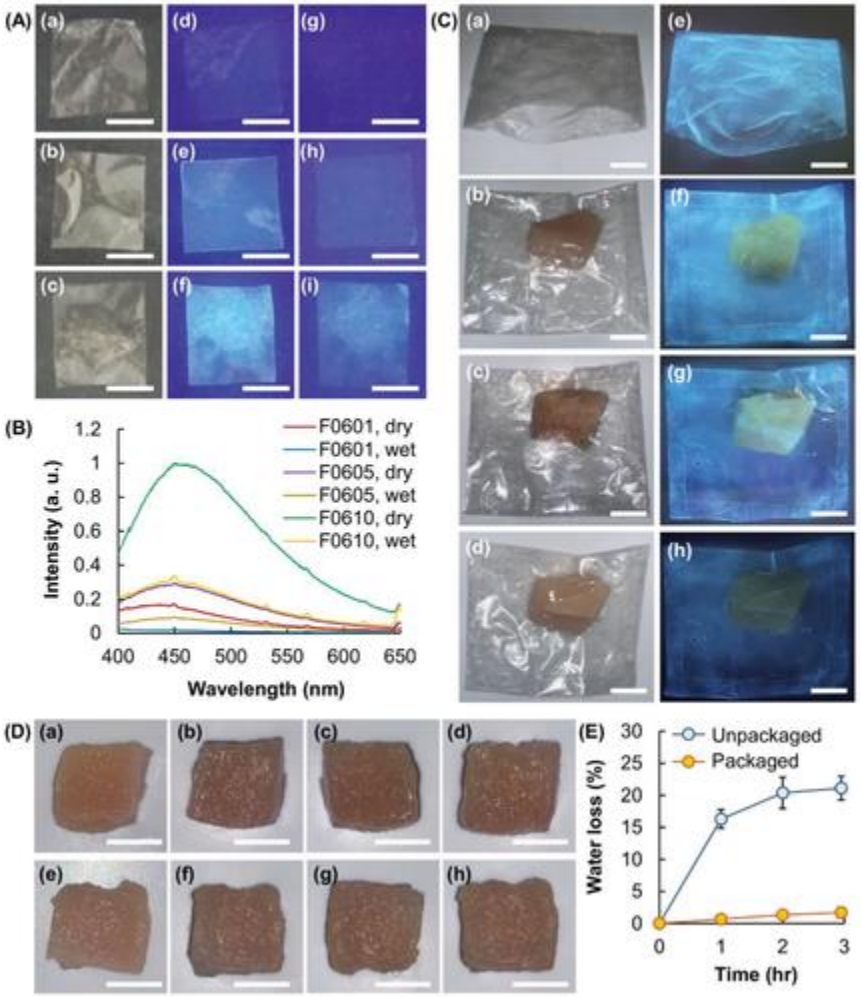

Figure 6 A) Photos of (a,d,g) F0601, (b,e,h) F0605, and (c,f,i) F0610, in either the (a–f) dry state or the (g–i) swollen state, under (a–c) white light and (d–i) UV light. Scale bar = 1 cm. B) PL spectra of films in either the dry state or the wet state. C) Photos of (a,e) a bag generated from F0605, as well as the bag containing (b,f) fresh chicken meat, (c,g) frozen chicken meat, and (d,h) thawed frozen chicken meat, under (a–d) white light and (e–h) UV light. Scale bar = 1 cm. D) Photos of the chicken meat, (a–d) with or (e–h) without being packaged by using a bag generated from F0605, after (a,e) 0 h, (b,f) 1 h, (c,g) 2 h, and (d,h) 3 h. Scale bar = 1 cm. E) Changes in the water content of the meat, with or without being packaged by using a bag generated from F0605, over time.

3 Conclusions

This study reports the generation of translucent and flexible films from CT. The films display not only high mechanical strength, high biocompatibility, and high thermal stability but also tuneable permeability and good UV-barrier properties. In addition, CT films possess self-indicating properties, with the intensity of luminescence being able to indicate not only the thawing of a frozen food but also the barrier properties of the films. For future

research, changes in films properties (including oxygen permeability and mechanical strength), as well as the identity of chemicals possibly produced, during film degradation and aging will have to be studied to optimize the performance of the films in food packaging. Examining possible migration of substances from the films to different types of food products will also be helpful when determining the range of products to which the films can be applied. Nevertheless, taking the favorable properties (ranging from UV-barrier properties to self-indicating capacity) of the films as demonstrated in this study into consideration, it is envisaged that CT films have the potential to be developed into dually self-indicating packaging films that can extend the shelf-life of the packaged food by not only protecting the food from the effect of light but also by maintaining the composition of the packaging atmosphere via its tuneable permeability and wettability.

4 Experimental Section

Materials

4-Dimethylaminopyridine (DMAP), 1-chloro-2,3-epoxypropane, 2-methylpropenoic acid, and various other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA). CE06, CE15, and CE50 were obtained from Macklin (Shanghai, China). Dulbecco's Modified Eagle's Medium (DMEM; Gibco, Grand Island, USA), penicillin G-streptomycin sulphate (Life Technologies Corporation, Chicago, USA), and fetal bovine serum (FBS; Hangzhou Sijiqing Biological Engineering Materials Co, Hangzhou, China) were used as the cell culture medium. Trypsin-EDTA (0.25% trypsin-EDTA) was obtained from Invitrogen (Carlsbad, CA, USA).

Film Production

CT was generated as previously described.[8] An appropriate amount of CT was dissolved in 50% v/v ethanol to reach a desired concentration. 10 mL of the solution was drop-casted onto a cleaned glass surface with the dimension of 10 cm x 10 cm. The glass slide was kept in vacuum at 40 °C for 10 h till the complete evaporation of the solvent. Films generated from a 1% w/v CT06 solution, a 5% w/v CT06 solution, a 10% w/v CT06 solution, a 5% CT15 w/v solution, or a 5% w/v CT50 solution were designated as F0601, F0605, F0610, F1505, and F5005, respectively.

Structural Characterization

Structures of CT and the generated films were characterized by using a FT-IR spectrometer (Nicolet5700; Thermo Nicolet Company, Waltham, MA, USA) at ambient conditions. Spectra were reported as an average of 16 scans.

Contact Angle Measurement

Sessile drop contact angle analysis of the films was performed using a video-based contact angle measurement system (OCA20; DataPhysics Instruments GmbH, Filderstadt, Germany) incorporated with a software-controlled dosing volume weight-drop. All measurements were performed by using water.

PL Characterization

PL characterization was performed by using a FLS920P fluorescence spectrometer (Edinburgh Instruments Ltd., UK). PL spectra were taken at the excitation wavelength of 370 nm. PLE spectra were taken at a fixed emission wavelength of 450 nm.

UV–vis Spectrometry

Transmittance spectra of the films were recorded at ambient conditions in the range 200–700 nm by using an UV–vis spectrophotometer (Jasco V-560; Jasco Co., Ltd., Tokyo, Japan) equipped with a quartz window plate. A holder in the vertical position was adopted during measurement. The UV block factor was calculated by dividing the average transmission at 400–700 nm by the transmission at 350 nm as previously reported.[23]

GPC

100 mg of CT06, CT15 or CT50 was dissolved in 10 mL of tetrahydrofuran (THF), which was adopted as a mobile phase during subsequent GPC analysis. The flow rate of the mobile phase was set as 1.0 mL min^{-1} during analysis. Dissolution detection was performed by using a refractive index detector at ambient conditions.

Film Thickness Measurement

Film thickness was measured by using a hand-held digital micrometer (Mitutoyo, Mitutoyo Corporation, Japan) with an accuracy of 0.001 mm, and was reported as an average value of ten measurements made at ten randomly selected locations of a film sample.

TGA

TGA and DTG of the films were performed by using a Q50 TGA (TA Instruments, New Castle, Delaware, USA) equipped with platinum pans. The study was done in an inert atmosphere of nitrogen from 40 to 600 °C. The heating rate was uniform in all cases and was set as 10 °C min^{-1}.

Tensile Strength

Films were prepared in a rectangular shape (width = 1.5, length = 5 cm). Their tensile strength was determined by using a tensile tester (M350-10CT; Testometric Co., Ltd., Rochdale, Lancashire, UK). During analysis, the films were subjected to a strain rate of 30 mm min^{-1} until breakage occurred. Each measurement was made in triplicate.

SEM Analysis

Films were sputter-coated with gold. Their microstructures were observed by using a JEOL JSM-6380 (Japan) microscope operated at an accelerating voltage of 10 kV.

Evaluation of the EWC

0.05 g of a film was immersed in 100 mL of distilled water. At various time intervals, excessive surface water was removed from the film using filter paper, followed by the determination of the weight of the swollen film. The procedure was repeated until no further increase in the film weight was observed. The EWC of the film was calculated by using the following equation:

$$EWC(\%)=[(ms-md)/ms] \times 100\%$$

where m_s and m_d represent the mass of the swollen film and that of the dried film, respectively.

Evaluation of Moisture Preservation

Mature Gala apples were purchased from a local store (Renrenle, Shenzhen, China). Each apple was cut into twelve pieces with a similar weight (8.5 ± 0.5 g). Each piece was put into a 50 mL centrifuge tube, with a hole of a diameter of 1.5 cm being drilled into the cap of the tube. The hole was covered by a film affixed to the cap. One tube in which the hole was uncovered was used as the control. All tubes were kept at 4 ± 1 °C. The weight of the tube was measured at regular time intervals. Each measurement was made in triplicate.

In Vitro Toxicity Assessment

HepG2 and HEK293 cells were cultured in DMEM supplemented with 10% FBS, 100 UI mL^{-1} penicillin, 100 µg mL^{-1} streptomycin, and 2×10^{-3} M L-glutamine. 24 h before the assay, cells were seeded separately in a 96-well plate at an initial density of 10 000 cells per well, and were incubated under a humidified atmosphere of 5% CO_2 at 37 °C. On the other hand, an appropriate amount of a film was ground using mortar and pestle, and was re-suspended in a fresh cell culture medium to obtain a suspension with a desired concentration. The suspension was filtered by using a 0.45-µm polytetrafluoroethylene (PTFE) filter (Advantec Co., Ltd., Japan). During the experiment, the cell culture medium in each well was replaced with 100 µL of the filtrate. After 5 h incubation at 37 °C, the filtrate in each well was replaced with the fresh cell culture medium. The CellTiter 96 AQueous nonradioactive cell proliferation assay (MTS assay; Promega Corp., Madison, WI, USA) was performed, according to the manufacturer's instructions, either immediately or after 24 h of post-treatment incubation.

In Vivo Toxicity Assessment

BALB/c nude mice (5 weeks of age) were purchased from the Institute of Laboratory Animal Sciences (Beijing, China). F1505 was dissolved in DMSO, which was selected as a solvent because of its track record of use in direct injection in preclinical trials,[8] to generate a 5% w/v solution. The solution was injected intraperitoneally into the mice, with the dose of CT being 20 mg kg^{-1}. The mice were weighed daily for one week. The solvent alone was used as the control. Seven mice were adopted for each treatment group. The procedures were approved by the Hong Kong Polytechnic University Animal Subjects Ethics Subcommittee, and were conducted in accordance with the Institutional Guidelines and Animal Ordinance of the Department of Health.

Performance Assessment for Food Packaging

Boneless skinless chicken breasts were purchased from a local store (Renrenle, Shenzhen, China), and were cut into rectangular pieces with similar surface area (≈3.5 cm^2). The meat was either placed directly under ambient conditions, or put inside a bag, which was generated by using F0605 with a dimension of 5 cm x 5 cm, before placing under ambient conditions. The meat was weighed at pre-set time intervals. Changes in the luminescence of a bag, in which meat samples in different states (viz., fresh meat, frozen meat, and thawed frozen meat) were put, was captured using a digital camera.

Statistical Analysis

All data were expressed as the means ± SD. Unless otherwise specified, the mean value was obtained by averaging three replicates. Student's *t*-test was performed to assess the statistical significance. Differences with p-value < 0.05 were considered to be statistically significant. Statistical analysis was performed by using GraphPad Prism 8.2.0 software (GraphPad Software Inc., USA).

Acknowledgements

This work was supported by Research Grants Council of the Government of Hong Kong Special Administrative Region (C5012-15E), and the Chinese University of Hong Kong, Shenzhen (PF01001421 and UDF01001421).

Conflict of Interest

The authors declare no conflict of interest.

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