SUPPORTING INFORMATION

Layer-by-Layer Assembly of Polysaccharide Films with Self-Healing and Antifogging Properties for Food Packaging Applications

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Synthesis and characterization of acrylamide-modified chitosan

The acrylamide-modified chitosan (AMCS) was prepared by one-pot reaction according to the literature.¹ Briefly, chitosan powder was dissolved in the KOH/LiOH/urea mixture by freezing-thawing method and then transparent chitosan solution was received.² The AMCS3 was obtained when the molar ratio of acrylamide to chitosan unit was set to 3. In detail, weighted acrylamide powder was added to 3 wt% chitosan solution (100 g) and the obtained mixture was stirred at 15 °C for 24 h. Then, HCl aqueous solution was used to neutralize the resulting alkaline mixture. After dialysis against ultrapure water for 7 days (50000-60000 cut-off), the white acrylamide-modified chitosan coded as AMCS3 was obtained by freeze drying.

The process to synthesis acrylamide-modified chitosan (AMCS) is shown in Fig. S1 (a). Upon the modification by acrylamide, amide groups were introduced into the unit of chitosan. Because they were unstable in KOH/LiOH/urea mixture, amide groups could further hydrolyze into carboxyl groups. The presence of acylamino groups and carboxyl groups on AMCS3 has been verified by FT-IR and ¹H-NMR. AMCS3 was dissolved in 1% hydrochloric acid to pronounce the carboxyl groups. Fig. S1 (b) showed the FT-IR spectra of chitosan and AMCS3 at low pH condition. Compared with the spectra of chitosan, a new peak at 1720 cm⁻¹ appeared in AMCS3 that dissolved in acid condition. The peak was attributed to the symmetrical stretching of – COOH groups. This peak primarily proved that chitosan had been successfully reacted with acrylamide in the alkali solution.

The degree of substitution of AMCS3 was obtained by ¹H-NMR characterization.¹ As shown in Fig. S1 (c) of ¹H-NMR spectra of AMCS3. The peaks at 1.92 ppm was assigned to the three acetamido protons. The peak at δ =2.43 ppm was assigned to protons of methylene that connected to carboxyl groups. The peak at δ =2.56 ppm was assigned to protons of methylene that connected to acylamino group. The peak at δ =3.04 ppm was assigned to the protons of methine that connected to amino groups of the deacetylated chitosan. The peaks between 3.40 ppm and 3.90 ppm were assign to H-3, H-4, H-5, H-6, H-6'. The peaks between 4.39 ppm and 4.42 ppm were assign to H-1of the acetylated chitosan. The degree of substitution of AMCS3 was evaluated by the following formula DS= 1/2*I(COO +CONH) /I(H1A+H2D) as previous literature reported.³ According to the ¹H-NMR spectra, the substitution of acrylamino groups and carboxyl groups was found to be 0.54.¹

The XPS O1s narrow scans of AMCS3 were shown in Fig. S1 (d). The difference between AMCS3 and chitosan was that AMCS3 was imparted with C=O (carboxyl groups) because of the modification by acrylamide. The XPS O1s narrow scans of AMCS3 displayed three peaks, which corresponded to C=Q (530.85 eV),⁴ C-QH (531.74 eV) and Q-C-Q (532.40 eV), respectively. The ratio of O element in AMCS3 to that in C=Q species from XPS survey scan of AMCS3 was found to be 6.48, which was in agreement with the theoretical value of 6~7. In addition, the ratio of C/N was 8.60, less than theoretical value 9. This could be explained that the degree of modification of chitosan was below 1, manifesting that free chitosan might be present in the obtained AMCS3 samples. The survey of scanning of AMCS3 can be found in Fig. S3. The FT-IR, ¹H-NMR, and XPS spectra of AMCS3 demonstrated the successful modification of chitosan. The weight-average molecular weight (M_w) of AMCS3 was 2.1×10^5 , which was determined by Gel Permeation Chromatography (GPC) according to the literature.⁵



Fig. S1 (a) Homogenous modification of chitosan with acrylamide in LiOH/KOH/urea mixture. (b) FT-IR spectra of chitosan (CS) and acrylamide-modified chitosan (AMCS3) at acid pH (1.0). (c)¹H-NMR spectra of AMCS. (d) O 1s spectra of AMCS3.

Synthesis and characterization of alginate aldehyde

The alginate dialdehyde (ADA) with a degree of oxidation of 50% coded as ADA50 was prepared according to the literature.¹ Briefly, 10 g sodium alginate was added into 200 mL ultrapure water, resulting in a 5 wt% alginate solution. 5.404 g sodium periodate was dissolved in 50 mL ultrapure water, and the two solutions were mixed at room temperature. Then, the above mixture was stirred in dark for 6 hours before 3.5 mL ethylene glycol was added into the solution with stirring for 30 min to terminate the reaction. The resulted solution was dialyzed against ultrapure water for 7 days to remove the remaining periodate. Finally, the ADA50 powder was obtained by freeze drying.

The synthesize procedure and characterization of ADA 50 are shown in Fig. S2. Fig. S2 (a) showed the introduction of ADA50. Fig. S2 (b) showed the FT-IR spectra of

the alginate and ADA50. As shown in Fig. S2 (b), in the spectra of alginate, the peaks at 795 cm⁻¹~965 cm⁻¹ (C-O-C) were distinctly strong. On the contrary, these peaks weakened in the spectra of ADA50, which corresponds to the literature.¹ This indicates the ring of repetitive unit of alginate opened as a result of the hydroxyl groups on C2 and C3 being oxidized into two aldehyde groups.⁶ The spectra changes therefore proved the preparation of ADA50.

Fig. S2 (c) displayed the XPS spectra of ADA50. In alginate repetitive unit, O element could only take part in C-OH, COONa, and O-C-O species, making it possible to define ADA50 by detecting the presence of CHO. However, the drawback of the peaks of CHO and COONa overlapping with each other may hinder its practicality. Fortunately, C1s of ADA50 could be used to indirectly prove the oxidation of alginate. The C1s of ADA50 demanded four peaks for curve fitting, 284.73 eV (C-C), 286.41 eV (C-O), 287.98 eV (O-C-O), and 288.96 eV (COOH), which agreed with the report in alginate dialdehyde.⁷ It's clear that the amount of C–O species in alginate would decrease while O-C-O species remain unchanged as the oxidation occurs. The literature reported that the ratio of C–O/O–C–O decreased from 1.8 in alginate to 1.2 in 50-ADA.⁷ Note that the ratio of C–O/O–C–O of ADA50 in the present study was 1.15, which means the -OH in alginate has been oxidized into aldehyde groups. The survey of scanning of ADA50 can be found in Fig. S3. In short, the results of FTIR and XPS spectra proved the preparation of ADA50. The M_w of ADA50 was also determined by GPC method. The concentration of ADA50 sample was 1 mg/ml. The M_w of ADA50 was determined to be 4.8×10^4 .



Fig. S2 (a) Schematic illustration of the process to synthesize oxidized alginate. (b) FT-IR spectra of original alginate and ADA50. (c) O1s spectra of ADA50. (d) C1s spectra of ADA50.



Figure S3. XPS surveys of ADA50, AMCS3 and [ADA50/AMCS3]₆ film.

Oxidation degree (OD) of sodium alginate was determined by Ultraviolet–Visible (UV-vis) Spectroscopy method by recording the absorbance changes,⁶ which mainly detects the assumption of NaIO₄ in the oxidation process. In the three repetitive experiments, before adding ethylene glycol, 1.00 mL oxidation reaction solution was taken out and diluted to 250 mL with ultrapure water. Then 3.00 mL of the dilution was mixed with 1.50 mL of indicator solution (mixture of 20% (w/v) KI and 1% (w/v) soluble starch solutions by equal volume, buffer phosphate pH 7 is solvent) and then the volume was completed to 5.00 mL with ultrapure water. UV-3600 spectrophotometer was used to quickly measure the absorbance of triiodine–starch complex at 486 nm. The periodate concentration in the sample was recorded using the molar absorption coefficient previously calculated from absorbance of the complex versus IO₄⁻ concentration. The difference between initial and final amount of IO₄⁻ corresponds to glycol moieties transformed into aldehyde groups. OD of sodium alginate was defined by the following equation:

$$OD = (m_1/214)/(m_2/198) \times 100\% = 198 \times m_1/m_2 \times 214 \times 100\%$$
(1)

Where m_1 and m_2 are the weight of sodium periodate and sodium alginate, respectively.

According to the UV–Vis characterization of ADA50, OD of sodium alginate was 46.45%.



Figure S4. SEM images of the cross section of $[ADA50/AMCS3]_n$ films: (a) 3 bilayers, (b) 6 bilayers, (c) 9 bilayers, (d) 12 bilayers, and (e) 15 bilayers. (f) Surface of $[ADA50/AMCS3]_6$ film.

number of bilayers	3	6	9	12	15
thickness/µm	0.6±0.10	1.2±0.06	1.7±0.06	2.1±0.07	2.7±0.05
healing cycles	3	4	5	6	7

Table S1. Healing cycles of $[ADA50/AMCS3]_n$ films.



Figure S5. Microscope images of a [ADA50/AMCS3]₁₅ film for the first (a, b), second (c, d), third (e, f), fourth (g, h), fifth (i, j), sixth (k, l), seventh (m, n) and eighth (o, p) cycles of damage/healing process. The spots were marked for location.

As shown in Figure S6, the[ADA50/AMCS3]₁₅ film exhibited no obvious selfhealing behavior at 98%RH for 120 h.



Figure S6. Microscope images of the Self-healing process of [ADA50/AMCS3]₁₅ film at 98%RH. (a) the fresh damaged film, (b) healing for 1 h, (c) healing for 120 h.



Figure S7. Water contact angle of (a) bare glass and glass that coated with (b) 3 bilayers, (c)6 bilayers, (d)9 bilayers, (e)12 bilayers and (f) 15 bilayers recorded at 5s.

As shown in Figure S8a-b, the fog formed on the bare glass became heavier from 5s to 10s as water drops in the surroundings continued to condense on the glass, then the fog gradually disappeared until about 60-70 s since water evaporation occurs.



Figure S8. Antifogging images of bare glass and double coated (by [ADA50/AMCS3]₆ film) glass recorded at (a) 5 s, (b) 10s, (c) 20s, (d) 30s, (e) 40s, (f) 50s, (g) 60s and (h) 70s.

As shown in Figure S9, the antifogging performance of the same glass that double coated with [ADA50/AMCS3]₃ film and [ADA50/AMCS3]₆ film is similar to the fog resistant behavior of films coated on separate glass (Figure 5b), which means glass of the same type doesn't influence the antifogging ability of the hydrophilic films very much.



Figure S9. Antifogging performance of the same glass that double coated with [ADA50/AMCS3]₃ film (upper) and [ADA50/AMCS3]₆ film (lower) recorded at (a) 5s, (b)10s and (c) 20s.

As shown in Figure S10a-b, the $[ADA50/AMCS3]_6$ film could heal the cut when PE film was used as a substrate.



Figure S10. Microscope images of the Self-healing behavior of [ADA50/AMCS3]₆ film on PE substrate. (a) damaged film, (b) self-healed film.



After abrasionHealedFigure S11. Microscope images of [ADA50/AMCS3]6 film. (a) abraded film (b)

healed film.

As shown in Figure S12, the transmittance of the film abraded for 13 times is 79%-82% from 380 nm to 780 nm.



Figure S12. Transmittance difference of the [ADA50 /AMCS3]₆ film coated glass for various number of abrasion tests.

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