This is the peer reviewed version of the following article: [Recent advances in self-healing materials for food packaging. Packaging Technology and Science 36, 3 p157-169 (2023)], which has been published in final form at https://doi.org/10.1002/pts.2701.

Recent advances in self-healing materials for food packaging

Kehao Huang[1], Yixiang Wang[1*]

[1]Department of Food Science and Agricultural Chemistry, McGill University, Ste Anne de Bellevue, Quebec, H9X 3V9, Canada

Kehao Huang, kehao.huang@mail.mcgill.ca

*Corresponding author: yixiang.wang@mcgill.ca

Abstract

Food packaging materials are often inevitably and imperceptibly damaged during the transportation, handling, and storage, and the disruption of their integrity poses a challenge to food preservation. Food packaging materials with self-healing capability can automatically repair the damaged areas and reconstruct original properties to avoid degradation of food quality and loss of nutrients. Various self-healing materials based on dynamic covalent bonds and/or dynamic non-covalent interactions have been developed and applied in food packaging in the forms of films and coatings at laboratory scale, and more efforts are required for the commercialization of these novel smart packaging materials. This is the first review to summarize the recent progress in the preparation of self-healing packaging materials through different mechanisms, compare the self-healing efficiency under different conditions, and highlight the potential applications of self-healing films and coatings with recoverable mechanical and barrier properties and other functionalities (e.g. antimicrobial and anti-fogging capacities). Finally, the future opportunities and challenges of applying self-healing materials in food packaging are described.

Keywords: self-healing, mechanisms, food packaging, functional materials

1 Introduction

Food packaging is imperative and a reality of modern living to maintain food quality and safety by protecting food products from influences of the external environment. However, food packaging materials are susceptible to damage during transportation, handling, and storage, posing a huge potential threat to food safety and challenging the future development of the food industry.[1] Therefore, it is necessary to continuously monitor damage and maintain the integrity of packaging material, but the repairing, recoating and replacing are costly and time-consuming.[2] In addition, pinholes and microcracks in packaging materials that are not observable to the human eye make it difficult to assess the integrity of packaging materials, affecting their barrier properties and further impairing the shelf life of foods.[3,4]

As an innovative type of materials developed in recent years, self-healing materials are naturally inspired by the ability of living systems such as skin, tissue, and bone to repair themselves, recognizing and repairing damage to re-establish their original properties, while extending the function of the material and maintaining its integrity, consistency and effectiveness.[5-7] The first attempts at self-healing materials were found in buildings constructed by the ancient Romans 2000 years ago, resisting microcracks in concrete by in situ crystallization of a durable mineral.[8] Laminates of aluminum foil and polyvinyl acetate fabricated by Malinskii et al. were the first study on self-healing materials.[9] In 2007, the first international conference on self-healing materials, organized by Sybrand van der Zwaag, provided a concept of self-healing materials with potential applications to all materials.[10] This discussion contributed significantly to the exchange of knowledge and accelerated the development of self-healing materials. Currently, the self-healing ability of packaging materials can be categorized into two types: intrinsic and extrinsic.[11] The intrinsic self-healing process is performed based on the reconstruction of chemical bonding of the matrix itself, including dynamic non-covalent interactions such as hydrogen bonds,[12] host-guest interaction,[13] electrostatic interaction,[14] π-π stacking,[15] and dynamic covalent interactions such as imine bonds,[16] acylhydrazone bonds,[17] Diels-Alder reaction,[18] retro-Diels-Alder reactions,[19] etc. The

extrinsic self-healing process in food packaging is achieved by capillary action in microcapsules, which repairs damage by releasing the healing agent from the incorporated container into the matrix.[1] Current research directions suggest that the intrinsic self-healing mechanism is more suitable for food packaging due to the absence of external healing agents, avoiding the complex design and extra cost of self-healing systems in the form of microcapsules.[20-23] According to the search results of Web of Science, 12,438 research papers on self-healing materials have been published from 2016 to 2022, of which 192 papers (1.54%) mentioned the potential applications in the food industry and 12 studies (0.096%) involved real food products. Currently, the real applications of self-healing food packaging materials are mainly restricted by the cost and complexity of materials involved in the manufacturing process and the fact that the required conditions to stimulate the self-healing process, such as high temperature and/or high humidity, may lead to the deterioration of food quality. Overall, self-healing materials for food packaging applications are a relatively new topic but have great potential. Hitherto, different forms of self-healing materials have been reported, such as fibers,[24,25] hydrogels,[26-28] microcapsules,[22] films,[29-31] and coatings.[14,32] Among them, self-healable fibers with high aspect ratios are commonly applied for producing batteries.[33] Self-healing hydrogels are 3D networks of hydrophilic polymers and can be developed for human motion detection,[34] wound dressing,[35] and battery applications,[36] while self-healable microcapsules contain the encapsulated healing agents in the wall material with a spherical shape and have been applied for dental,[37] aerospace coatings,[38] and paints.[39] Films and coatings are the main forms of self-healing materials reported in recent years for food packaging. They can share similar formulations, but the coatings are directly applied on the surface of food and the films are prepared independently by casting or freeze drying. This review is the first attempt to summarize the recently developed self-healing materials and their potential applications in food packaging. The future opportunities, challenges and research directions are described.

2 Self-healing mechanisms

The design of self-healing materials is intimately associated with their applications to

the form of food packaging, and is generally governed by the following principles: (1) the applied materials with self-healing ability should be economic and non-toxic, and have an insignificant effect on the taste and texture of the food; (2) the self-healing reactions should occur autonomously or be in response to an external stimulus; and (3) the self-healing reactions should simultaneously repair both morphological and functional properties of the packaging materials.[40,41] Both dynamic non-covalent and covalent interactions can be used to fabricate self-healing materials for food packaging. Dynamic non-covalent bonds can be effectively repaired with little or no external energy at room temperature, but they are mechanically weaker than dynamic covalent bonds due to their weak intermolecular forces and reversible interactions.[40,42,43] Simultaneous and continuous reversible assembly and decomposition of dynamic covalent bonding systems usually occur in response to light, heat, and force, and the produced self-healing materials can exhibit high stability even after the removal of external stimuli.[44,45]

2.1 Dynamic non-covalent bonds

2.1.1 Hydrogen bond

Hydrogen bonds are formed between hydrogen atoms and highly electronegative atoms, such as nitrogen, oxygen, and fluorine. Several studies have reported the fabrication of self-healing materials from chitosan,[46] starch,[47] carrageenan,[48] and protein[49] by hydrogen bonds. The self-healing efficiency is related to the amount of hydrogen bonds in polymer matrix. For instance, poly(vinyl alcohol) (PVA) is abundant in hydroxyl moieties that contribute to a good gelling and film-forming capacity with self-healing ability.[50] Liu et al.[12] optimized the weight ratio of PVA and cellulose nanocrystals (CNC) to 60:1 to maximize the self-healing efficiency (37.03%) of PVA-based hydrogels. The inadequate amount of free hydroxyl groups at low PVA content led to weak hydrogen bonding ability, and the excessive PVA reduced the mobility of molecules and decreased the self-healing efficiency.[51] However, hydrogen bonds are relatively weak, so the resultant self-healing materials usually exhibit weak mechanical properties. This

could be improved by the addition of cross-linking agents. For example, increasing the concentration of carboxymethyl chitosan (CMCS) from 0% to 1.3% enhanced the tensile strength of cross-linked hydrogels of aluminum ions (Al^{3+}) and polyacrylic acid (PAA) from 83.1 kPa to 149.2 kPa and tensile strain from 1673% to 1722% with no disruption of self-healing ability of hydrogels (92.9% of stress and 98.8% of strain after 24 h of healing at 25 ℃).[52] For hydrogels formed by cross-linked networks of 2-ureido-4-pyrimidone monomer, acrylamide and acrylic acid, the increase in acrylic acid content from 10% to 20% improved the tensile strength and elastic modulus from 3.02 MPa to 6.54 MPa and 0.53 MPa to 2.93 MPa, respectively.[53] It was worth noting that the cross-linking resulted in the enhanced mechanical properties, but additional energy was also required for the breakage and re-construction of polymer networks, leading to the weakened self-healing ability. Recently, a strategy of forming multiple hydrogen bonds has been applied to produce strong self-healing materials. For instance, Zhu et al.[54] were inspired by nacre and mussels and fabricated an ultrarobust self-healing composite material by establishing quadruple hydrogen bonds between dopamine-modified graphene oxide and polyurethane prepolymer, which showed 90% self-healing efficiency at 25 ℃ in 1 h. Moreover, the synergistic effects of hydrogen bonds with other dynamic interactions such as acylhydrazone bonds[55,56] and Diels-Alder reaction[57,58] could also contribute to the enhancement of mechanical properties while maintaining the self-healing ability.

2.1.2 Hydrophobic interaction

Hydrophobic interaction has been used predominantly as an alternative strategy for the design and fabrication of self-healing hydrogels. For example, hydrophobic monomers were incorporated with hydrophilic monomers to form a hydrogel network through the micellar polymerization technique.[59] Tang et al.[60] synthesized amphiphilic metallopolymers to interact with hydrophobic metal coordination units, resulting in micelle aggregation followed by the formation of a stimuli-responsive hydrogel. Zhou et al.[61] proposed that $(NH_4)_2SO_4$ solution could improve the hydrophobic interactions among phenylboronic acid-modified gelatin, catechol-modified carboxymethyl

chitosan, 3,5-dinitrosalicylic acid, and Eu^{3+} ions, and temporary cross-linked regions could form to stabilize the shape of hydrogels. A simple one-pot method to fabricate dual physically cross-linked hydrogels based on the hydrophobic association and ionic interaction between sodium alginate (SA) and polyacrylamide (PAM) was reported by Zheng et al.[62] However, although the increased concentration of SA enhanced the fracture stress of composite hydrogels, it also restricted the movement of PAM segment and resulted in the unsatisfactory self-healing ability. Deng et al.[63] used the hydrophobic interaction between the sodium dodecyl sulfate (SDS) micelles and the alkyl groups of stearyl methacrylate (SMA) in PAM to construct self-healing hydrogels, which could quickly recover from stretching within 2 min at room temperature. However, the addition of carrageenan to these double cross-linked hydrogels improved the mechanical properties but decreased the self-healing efficiency due to the restricted movement of the molecular chains.

2.1.3 Electrostatic interaction

Reversible electrostatic interactions can be initiated between the charged polymers and ions,[52] polyelectrolytes,[64] polyampholytes,[65] and zwitterionic fusions,[66] resulting in the formation of self-healing films,[31] hydrogels,[12] and aerogels.[67] For instance, a polyelectrolyte multilayer (PEM) film with self-healing ability was constructed from polydopamine and SA by layer-by-layer (LBL) assembly.[68] Zhao et al.[67] manufactured an aerogel based on the electrostatic interactions between $-NH^{3+}$ of chitosan and $-COO^{-}$ of itaconic acid. A similar composite aerogel of chitosan and itaconic acid was constructed by the freeze-drying process, where the structure and mechanical properties of the cut aerogel could recover within 30 s at room temperature via wetting treatment.[69] Maiz-Fernández et al.[70] fabricated a hydrogel by forming electrostatic interactions between chitosan and hyaluronic acid, which showed complete self-healing after 15 min at room conditions. Similarly, electrostatic interactions were also combined with other cross-linking strategies to produce self-healing hydrogels. Fang et al.[71] used β-cyclodextrin (β-CD) and carboxymethyl cellulose (CMC) to prepare pH-sensitive hydrogels based on host-guest and electrostatic interactions. The existence of cationic

β-CD effectively increased the self-healing efficiency from 17% to 55% after 6 h, indicating the important role of electrostatic interaction in self-healing process. The antibacterial hydrogels with self-healing ability under acidic conditions were developed from aluminum ions, CMCS, and PAA.[52] During the self-healing process, hydrogen bonds were firstly reconstructed and Al^{3+} ions gradually diffused to the fracture interface simultaneously with chitosan, promoting the reconstruction of coordination bonds and electrostatic interactions.

2.1.4 Host-guest interaction

Host-guest interaction is formed when the guest moieties are physically inserted and combined with the host moieties. Common host molecules include CD, crown ethers, cucurbiturils, cuproaromatics, etc.,[72,73] where CD is widely used because it is non-toxic, easy to synthesize, and has a hydrophobic cavity to bind hydrophobic guests.[28] Yang et al.[28] investigated the host-guest interaction between l-menthol and β-CD. The damaged coating swelled under the stimulus of water, which prompted the contact of free groups and self-healed within 20 min. Peng et al.[74] disclosed the principle of self-healing by host-guest interaction: upon contact with moisture, the broken interfaces swell and contact with each other, so the free host-guest molecules are reintegrated. A self-healing coating with UV shielding property was produced from β-CD, TiO_2 and 2-hydroxyethyl methacrylate and applied on the surface of food packaging materials to prevent from oxidation. Mohamadhoseini et al.[73] provided an in-depth comparison of the interactions between different guest molecules and CD and their effects on the self-healing efficiency and stimulus responsiveness. The association constants of CD and guest molecules determined the self-healing efficiency. Compared with azobenzene (1×10^4), ferrocene (1.7×10^4), and cholic acid (4×10^3), adamantane (AD) possessed the highest association constant (3.5×10^4). β-CD and adamantane were then grafted on the backbone of alginate as host and guest groups to construct self-healing hydrogels, and the self-healing process completed within 5 s, demonstrating the strong interactions between β-CD and adamantane.[75] Xuan et al.[76] contrasted the properties of PAA/poly (ethylenimine) (PEI) multilayer films and PAA-AD/PEI-β-CD LBL films, which were

formed by electrostatic interaction and host-guest interaction, respectively. The PAA-AD/PEI-β-CD films showed better transparency, mechanical properties, and stability in different pH environments.

2.2. Dynamic covalent bonds

2.2.1 Imine bond

Imine bond is a reversible covalent bond prepared by the facile condensation of an aldehyde or a ketone with primary amines.[77] Liu et al.[27] used dialdehyde debranched starch to react with chitosan to form Schiff base hydrogels with a gelation time of less than 30 s. The mechanical properties of produced hydrogels could be controlled by varying the molar ratio of amino group and aldehyde group and reaction temperature. Natural vanillin and chitosan were selected to fabricate the self-healing hydrogels,[16] and a balance between mechanical properties and self-healing ability was reached when the molecular ratio of aldehyde and amino groups was about 7:1. Further increase in vanillin content resulted in the fixed linkage of chitosan by massive hydrogen bonds, which reduced the imine bonds and self-healing capability. Pettignano et al.[78] disclosed that the gelation process and self-healing efficiency of hydrogels were related to the concentration, ratio, and type of biopolymers. Specifically, the increase in the weight ratio of oxidized SA and gelatin from 1:1 to 2:1 accelerated the self-healing process and resulted in the high resistance to stretch, while the increased concentration of biopolymers from 5% to 15% led to a more regular and cylindrical hydrogel. At the same time, since type B gelatin had a lower isoelectric point (pI) (4.7-5.2) than type A gelatin (7.0-9.0), type B gelatin could form a more stable hybrid network with faster self-healing process at pH 7.2. Yang et al.[79] prepared a self-healing hydrogel with a remarkable antioxidant activity using ε-poly(L-lysine) carbon dot (PL-CD) and oxidized dextran (ODA). Increasing PL-CD content led to a shorter self-healing process within 32 s, which was ascribed to the prompted Schiff base reaction by higher -NH_2 concentration. Wang et al.[80] synthesized a hydrogel from ABA triblock copolymer and polyethylenimine (PEI), which showed a self-healing process within 30 min and antimicrobial activity against both *Escherichia coli* and *S. aureus*, indicating its

potential application as an active food packaging material.

2.2.2 Acylhydrazone bond

Acylhydrazone bond is formed by the reaction of aldehyde and hydrazine groups under mild acidic environment (pH 4-7) or high-temperature catalytic environment,[81] which has similar structure but better stability than imine bond.[82] Chen et al.[17] produced the pectin achlydrazide based hydrogels with labile phenolic bond and acylhydrazone bond. The pore size of hydrogel was negatively correlated with the concentration of the aldehyde group, and the self-healing capability was limited in the slightly acidic environment (pH 4-6). Qiao et al.[55] used dialdehyde-terminated polyethylene glycol (PEG–CHO) and adipic dihydrazide-modified alginate (ALG-ADH) to produce self-healing hydrogels. The self-healing process was observed after 6 h without any external stimulation, which was attributed to the dynamic characteristics of acylhydrazone bonds and the reversibility of multiple hydrogen bonds. Huang et al.[83] constructed an antimicrobial hydrogel using oxidized cellulose acetoacetate to react with carboxymethyl chitosan and oxalyl dihydrazide, and the enamine linkages and acylhydrazone bonds enabled the self-healing process in 30 min. Zhu et al.[84] illustrated the effect of metal coordination bond on the self-healing efficiency by the incorporation of Fe_3O_4. The composite hydrogel made of PAM, oxidized alginate, and cellulose nanocrystals showed a fast closing of cracks within 10 min, while the addition of Fe_3O_4 accelerated the healing speed to few seconds. Moreover, compared to the Fe_3O_4-free hydrogel, the ionic hydrogels did not exhibit any obvious loss of water after one week, which demonstrated the better stability and ensured self-healing capability.

2.2.3 Diels-Alder (DA) reaction

DA reaction is a click electrocyclic reaction between a conjugated diene and a dienophile with the advantages of high yield, high reaction selectivity, no side reactions, etc.[85-87] However, the self-healing process triggered by DA reaction is usually time-consuming and requires a heating condition. Cai et al.[88] reported the formation of self-healing coatings/films by the DA reaction between poly(lactic acid)-block-poly(2,5-furyl dimethylbutyrate) and bis(maleimide) triethylene glycol. The material with low

cross-linking density showed only 50% self-healing efficiency after 5 days at room temperature, while the films with optimized cross-linking density exhibited 96.3% self-healing efficiency in 5 min at a moderate heating condition (30 ℃). Recently, DA reaction was commonly combined with other reversible interactions to fabricate the materials with fast self-healing ability. Li et al.[18] prepared the composite hydrogels from furan-modified pectin and maleimide-modified chitosan, where the first stage of the self-healing process was due to the electrostatic interaction, and the network of hydrogels was formed by DA reactions in the second stage. A stiff UV-curable self-healing coating based on DA reaction and multiple hydrogen bonds was disclosed by Liu et al.[57] DA intermediate was formed by *N*,*N*'-(4, 4′-methylenediphenyl) bismaleimide (BMI) and furfuryl alcohol (FA), followed by the reaction with methacrylic acid isocyanate (IEM) to obtain the modified DA monomer. The self-healing coating was formulated with polyurethane (PU) pre-polymers, modified monomer, and initiator. By modifying the molecular weight of PU and the ratio of DA monomer to PU, the self-healing efficiency could be changed from 33% to 100% at 120 ℃ in 10 min.

2.2.4 Disulfide bond

Disulfide bond is formed with two mercaptans through either an exchange reaction or a metathesis reaction.[89] Disulfide exchange reaction is commonly used to produce self-healing hydrogels, since metathesis reaction requires a higher working temperature.[90] The exchange kinetics of disulfide bonds can be promoted under alkaline conditions and inhibited under acidic conditions.[91] Chang et al.[92] fabricated a transparent PU film by dissolving PU and 4–4-aminophenyl disulfide in *N*,*N*-dimethylformamide, but the self-healing behavior was only observed when the temperature was above 60 ℃. Jian et al.[90] manufactured a self-healing PU film based on disulfide metathesis reaction, in which 2-hydroxyethyl disulfide reacted with polytetramethylene ether glycol and 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate. The self-healing behavior was observed after 12 h at 60 ℃. The double cross-linking strategy combining disulfide bonds was also reported. For instance, Xia et al.[93] proposed an albumin-based double

cross-linked hydrogel with self-healing ability at 25 ℃. The exchange and rearrangement of disulfide bonds of albumin were triggered by glutathione, and tetrakis (hydroxymethyl) phosphonium sulfate was grafted to the amino groups of BSA via a Mannich-type reaction to form a double-cross-linked network. Wang et al.[94] prepared the self-healing hydrogels containing acylhydrazone bonds and disulfide bonds by cross-linking dialdehyde carboxymethyl cellulose (DCMC) and 3,3′-dithiobis(propionohydrazide), and investigated the effect of cellulose nanofibrils (CNF) on the properties of hydrogels. Since the acylhydrazone bonds predominated in the hydrogels, the increase in solid content and oxidation degree of DCMC shortened the gelation period and the healing of cracks happened in 1 h without any external force. Mredha et al.[95] constructed a multifunctional poly(disulfide)-based hydrogel by copolymerizing 2,3-dimercapto-1-propanol and meso-2,3-dimercaptosuccinic acid. The obtained hydrogels showed a fast self-healing behavior within 5 s at 25 ℃ in air or under water, which was due to the synergistic effect of dynamic disulfide bonds and the high density of hydrogen bonds and ionic bonds.

3 Potential applications of self-healing materials in food packaging

Self-healing materials provide a new way to design smart packaging.[96] Recently reported self-healing materials for food packaging are summarized in Table 1 and are usually in the forms of films and coatings. The self-healing process observed in films and coatings were summarized into Figure 1.

312 Table 1. Recently reported self-healing materials for food packaging applications.

Types	Compositions	Mechanisms	Self-healing efficiency	Recovery rate of functionalities	Refs
Films	CS-CA-CC	Hydrogen bonds	RT for 60 s	E: 56%; TS: 72%	[97]
	AMCS-ADA	Imine bonds	RT within 2 min	T: 82.1%	[29]
	MCNC-PVA	Hydrogen bonds	RT within 20 min	TS: 69.54%	[98]
	Aromatic disulfide based TPU	Disulfide bonds	/	/	[30]
	β-CD-PEI-adamantane-PAA	Host-guest interaction	RT within 30 min	E: 87.2%	[76]
	β-CD-PEI-PAA-Fc	Host-guest interaction; hydrogen bonds	RT within 30 min	E: 97.65%; TS: 74.67%	[99]
	PDA-SA-CAP-CS	Electrostatic interactions	RT for 24 h	/	[68]
	CMC-CS	Electrostatic interactions	RT for 10 min	/	[31]
	PEI-PAA	Electrostatic interactions	RT within 10 min	OTR: 100%	[100]
	PVA-PAA-Ag NPs	Hydrogen bonds	RT within 4 h	T: 97.76%	[101]
Coating	CS-Beeswax-Pollen grains	Hydrogen bonds	/	TS: 92%	[102]
	bPEI-PAA-$CaCl_2$-MMT	Electrostatic interactions	RT within 30 s	/	[103]
	SA-menthol-CD-CS	Host-guest interaction	RT within 20 min	TS: 59.49%	[28]
	PEI-β-CD-PAA-AD-C_3N_4	Host-guest interaction	RT within 30 min	/	[104]
	SA-CS	Hydrogen bonds; Electrostatic interactions	RT within 5 min	TS: 97%; OTR: 95%; WVP: 63%	[14]
	MoS_2-β-CD-PEI-AD-PAA	Host-guest interaction	RT within 30 min	/	[105]

313 Note: RT, room temperature; E, elongation; TS, tensile strength; T, transmittance; OTR,
314 oxygen transmission rate; WVP, water vapor permeability; CS, chitosan; CA, citric acid;
315 CC, choline chloride; AMCS, acrylamide-modified chitosan; ADA, alginate aldehyde;
316 MCNC, multi-branched cellulose nanocrystals; PVA, polyvinyl alcohol; TPU,
317 thermoplastic polyurethane; PEI, polyethyleneimine; Fc, ferrocene; PDA,
318 polydopamine; SA, sodium alginate; CAP, capsaicin; CMC, carboxy methylcellulose
319 sodium; bPEI, branched polyethyleneimine; MMT, sodium montmorillonite nanoclay;

CD, cyclodextrin; AD, adamantanamine; Ag NPs, silver nanoparticles

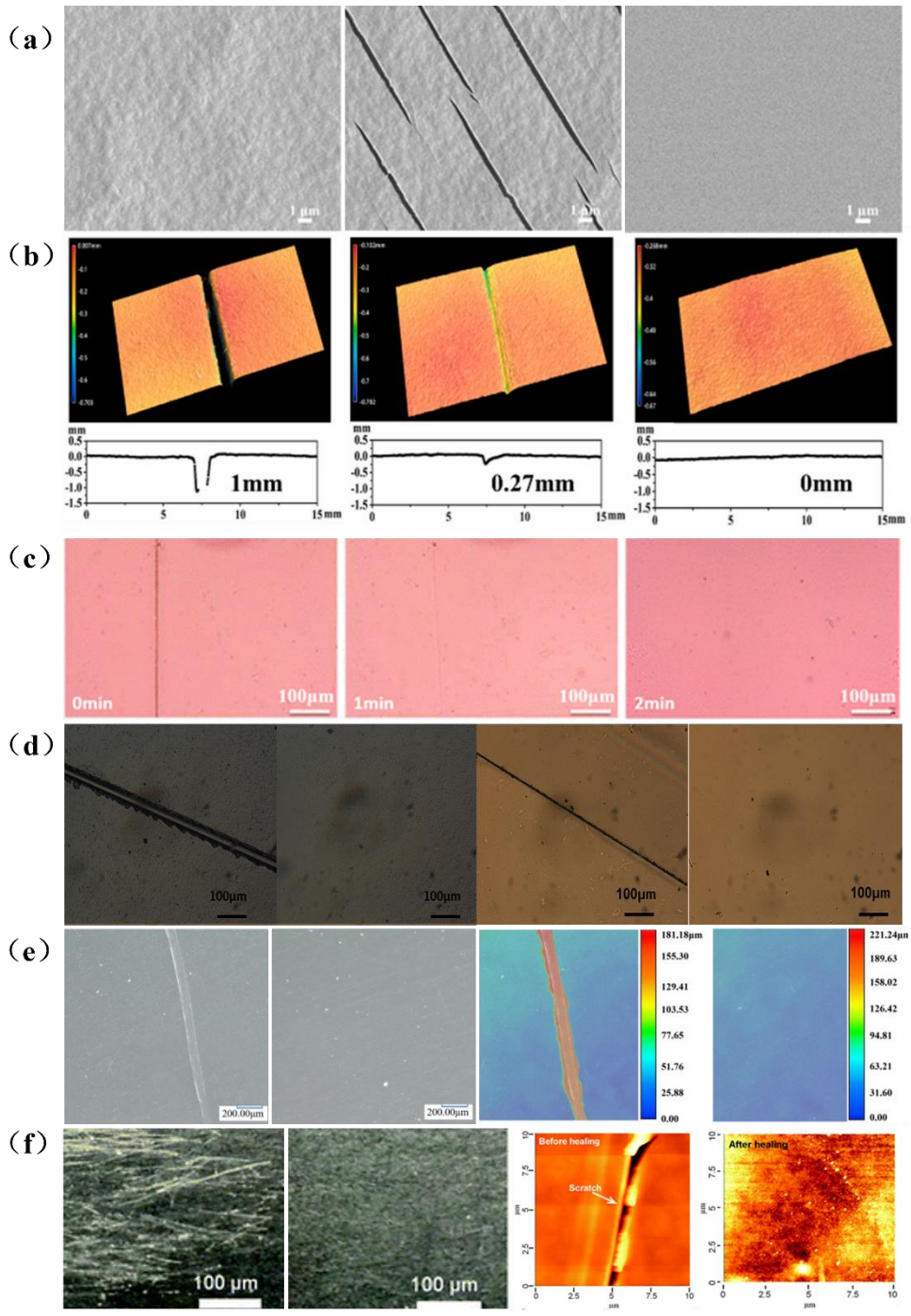


Figure 1. Self-healing of (a) damaged PEI/PAA film under 97% RH for 24h,[100] (b) PBS/LMMT composite film under room condition for 8 h,[106] (c) $[ADA50/AMCS3]_6$ film at room temperature for 2 min,[29] (d) scratched $[SA/CD\text{-}g\text{-}CS]_{10}$ and [SA/menthol-CD-g-CS]$_{10}$ in 20 min,[28] (e) scratched poly(SBMA-co-IA) coated glass at 25 ℃ and 55% RH for 6h,[107] (f) scratched PET/Pectin/TA coating over hot water (55 ℃ and 100% RH) for 60s.[108]

Note: PEI, polyethyleneimine; PAA, polyacrylic acid; PBS, polyborosiloxane; LMMT, L-cystine modified MMT nanosheets; ADA, alginate aldehyde; AMCS, acrylamide-modified chitosan; SA, sodium alginate; CD, cyclodextrins; CS, chitosan; SBMA, (methacryloyloxy)ethyldimethyl-(3-sulfopropyl); IA, itaconic acid; PET, poly(ethylene terephthalate); TA, tannic acid.

3.1 Self-healing films for food packaging

Accidental damage during handling and transportation may weaken the protective function of packaging materials. Therefore, self-healing films with recoverable mechanical and barrier properties are necessary to maintain food quality. Smirnov et al.[97] mixed chitosan with citric acid-based natural deep eutectic solvent (NADES) to prepare a self-healing film using the solution casting method. The damaged films were pressed by finger and healed within 60 seconds at room temperature. The healed films showed a strain of 47 ± 15% and a stress of 13 ± 2 MPa, with recovery rates of 56% and 72%, respectively. PEM films with super oxygen barrier property were constructed from PEI and PAA by Song et al.[100] The films could heal in a high humidity environment (>97%) within 10 min, but a humidity lower than 50% would not lead to the swelling of the damaged area and the self-healing. The films after ten stretching-healing cycles showed about 92% recovery of elastic modulus (13.09 ± 0.12 GPa) and excellent oxygen barrier property (<0.005 cm^3 m^{-2} d^{-1} atm^{-1}). Another self-healing nanocomposite films were manufactured from grafted cellulose nanocrystals (g-CNC), matrix prepolymers from monomers, dibutyltin dilaurate (DBTDL), and hexamethylene diisocyanate (HDI).[109] The dynamic hydrogen bonds and metal-ligand coordinated covalent bonds enabled the self-healing capacity at low temperature. The increase of g-CNC from 0 wt.% to 3 wt.% enhanced the covalent bonds and hydrogen bonds, resulting in 99% self-healing efficiency at 5 ℃ within 1 h. A self-healable hydrophobic cellulose film was assembled by incorporating natural wax through annealing treatment.[110] The annealing process at 150 ℃ promoted the rearrangement of wax in the cellulose matrix and the wax migrated to the surface of film to achieve self-healing. The incorporation of natural wax also increased the water contact angle (120°) and improved the flexibility (11%) without reducing mechanical strength (122 MPa) of cellulose films.

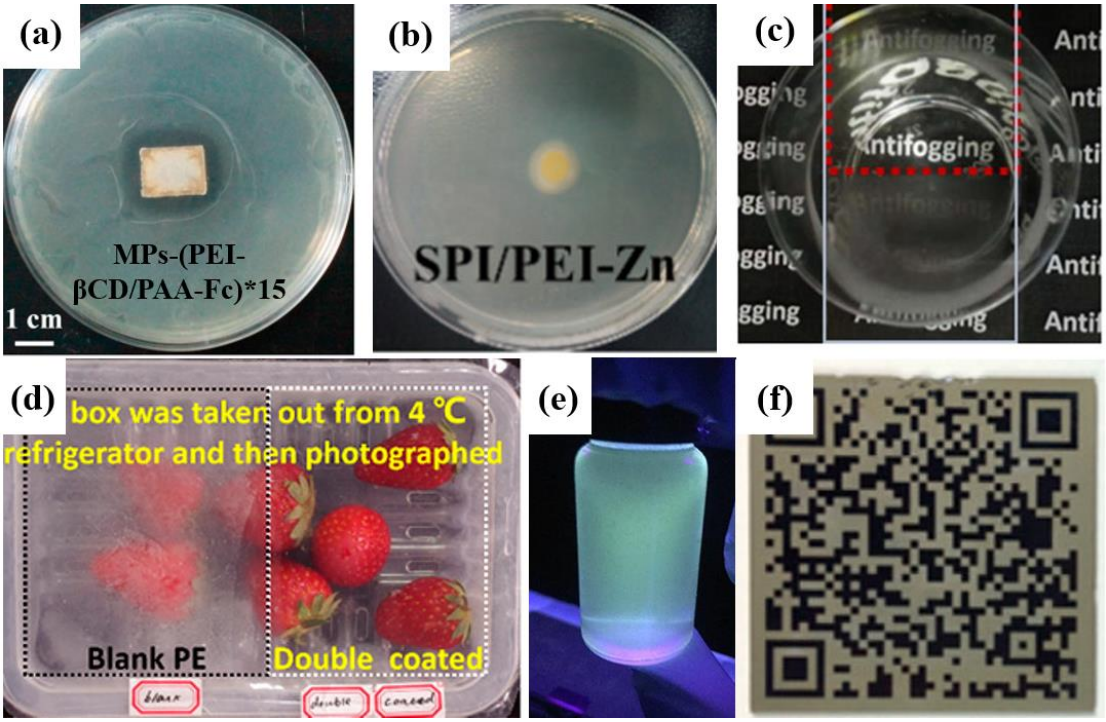


Figure 2. Self-healing packaging films with (a,b) antimicrobial, (c,d) anti-fogging, (e) heavy metal detection, and (f) recoverable labelling capacities.[29,99,101,111-113]

Other functionalities can also be integrated with the self-healing capacity for active packaging, and some recent examples are shown in Figure 2. Two metal ions (Cu^{2+} and Zn^{2+}) were added in the solution of soy protein isolate (SPI), PEI, and glycerol to fabricate the self-healing and antimicrobial films.[111] The highly branched structure and abundant amine groups in PEI easily disrupted the ordered structure of SPI and formed numerous hydrogen bonds. The incorporation of Cu^{2+} in the films led to better self-healing efficiency and antimicrobial activity than Zn^{2+}, which was attributed to more coordination bonds and stronger interaction between Cu^{2+} and negatively charged bacterial cell walls, respectively. The original films containing Cu^{2+} showed the tensile strain and stress of 81.78% and 10.09 MPa, which were recovered to about 90.17% and 105.57% after self-healing at 25 ℃ for 10 h. Xuan et al.[99] assembled dual cross-linked films consisting of PEI-β-CD and ferrocene-modified PAA with host-guest and hydrogen bonding interactions. The low water contact angle (31.8°) indicated the hydrophilic surface that facilitated the spreading and penetration of water into the films and led to the fast self-healing process. The maximum tensile force of the virgin film

was 0.75 N and the stretched length was 0.85 mm, which recovered to 0.56 N and 0.83 mm, respectively, after 30 min self-healing process. At the same time, the films loaded with microencapsulated chloramphenicol possessed a controlled release behavior to inhibit the growth of *E. coli*. Anti-fogging packaging films have been developed recently by LBL assembling of acrylamide-modified chitosan and alginate aldehyde with Schiff base reaction to enable the self-healing property and high transparency.[29] The recovery efficiency of light transmission of the healed film at 600 nm was 82.1% after 20 times of mechanical abrasions with a Taber abraser, indicating its favorable self-healing ability toward mild or heavy scratches. The anti-fogging ability was achieved by absorbing the condensed water in the hydrophilic films and the thicker films could better prevent from fogging. In another case[101], a simple one-pot method was used to prepare the PVA/PAA/Ag composite films with self-healing, anti-fogging, and antimicrobial properties. The scratched composite film returned to a smooth and integrated surface after the self-healing process (temperature & time) without any significant effect on its transmittance (slightly changed from 89.1% to 87.1%), which was due to the fluidity of the polymer chains and reforming of hydrogen bonds. The anti-fogging property was attributed to the abundant hydroxyl groups, while the addition of 2% silver nanoparticles results in 99% antibacterial effect against *E. coli*. An intelligent soy protein-based film was designed with self-healing ability and could detect potential contamination of food by heavy metals.[112] The addition of polydopamine (PDA) induced the dense cross-linked network with enhanced tensile strength and endowed the film with the capacity to detect heavy metals (>0.0032 mol/L) in food through fluorescent signals. The composite film showed the restorability at 50 ℃ and RH 60-70% within 30 min, which was attributed to the high flowability of amines of PEI and phenolic hydroxyl groups of dopamine. The healed film had the tensile stress of about 5.76 MPa and the strain of 85.95%, which were 92.46% and 75.43% of the original values, respectively. Interestingly, Chen et al.[113] assembled a photoreactive LBL film from PAA grafted with phenyl amino groups and PEI via a carbodiimide reaction for displaying recoverable QR code. The scratched QR code made from

composite film self-healed and became machine-readable in a RH 100% environment after 12 h. It was because the polyelectrolyte chains were highly activated at saturated humidity, and the subsequent interdiffusion of polyelectrolytes allowed the transfer of substances between sites and healed the scratches. This "smart" label material could be used for restorative graphic identification and information retention in food packaging.

3.2 Self-healing coatings for food packaging

The self-healing coatings can be applied directly to food surface to decrease water vapor transmission, control oxygen permeability, and prevent oxidation. As shown in Figure 3 (a), for instance, a composite coating from chitosan and beeswax–pollen grains was fabricated by Sultan et al.[102] The formation of electrostatic interactions and hydrogen bonds in the coating resulted in an improvement in water vapor barrier property (1038.07 g per m^2 per day), tensile (0.99 MPa), and self-healing efficiency (96.30%) compared to virgin chitosan films, which were 2065.23 g per m^2 per day, 0.77 MPa, and 86.70%, respectively. However, the oxygen transmission rate of the composite coating increased due to the addition of beeswax which increased the hydrophobicity of the film and more oxygen diffusion pathways. The coated pear showed extended shelf life of 105 days at 0 ℃ and one week at 23 ℃, maintaining the quality of pears during storage and marketing conditions. A PEM coating was fabricated by LBL assembly of CMC and chitosan, which significantly decreased the weight loss of apple slices and maintained the firmness and quality for 24 h.[114] The original coating had a tensile strength of 28.49 MPa, and the strength of the damaged coating restored to 24.9 MPa after self-healing for 20 min. This self-healing process was triggered by water and was ascribed to the formation of hydrogen bonds and electrostatic interactions between $-NH_3^+$ and $-COO^-$. Moreover, the addition of chitosan endowed the fabricated PEM coating with the free radical scavenging activity of 78.62%, and the antibacterial capacity of 100% and 95.48% against *Salmonella* and *E. coli*, respectively.[31] A similar PEM coating was manufactured from CMC, chitosan, and $CaCl_2$ for the storage of lemons under refrigerated conditions for up to 60 days.[115] It was revealed that the

increased thickness of coating contributed to the higher cross-linking degree and led to the enhanced gas barrier, mechanical, and self-healing properties. Specifically, when the number of bilayers increased from 3 to 7, the water vapor permeability decreased from 3.32 $g \cdot mm \cdot kPa^{-1} \cdot h^{-1} \cdot m^{-2}$ to 1.15 $g \cdot mm \cdot kPa^{-1} \cdot h^{-1} \cdot m^{-2}$, while the tensile strength enhanced from 18.08 MPa to 39.94 MPa and the self-healing efficiency improved from 83% to 92%. Du et al.[14] developed an edible coating with self-healing property through LBL assembly of chitosan and SA by hydrogen bonding and electrostatic interactions. The coating formed by three assembly cycles showed > 80% transparency and an insignificant impact on the appearance of packaged fruits and vegetables. The coating healed within 5 min under water stimulation and showed 97%, 95% and 63% recovery of tensile strength (19.89 MPa), oxygen transmission rate (4.78 ± 0.82 $cm^3/(m^2\ d\ atm)$), and water vapor transmission rate (40.56 ± 7.60 $g/(m^2\ d)$) to those of intact coating, so it could diminish the effect of coating damage and remarkably retard the deterioration of packaged strawberries. Manabe et al.[103] proposed a cephalopods-inspired rapid self-healing nanoclay composite coating with oxygen barrier and super-bubble-phobic properties. The LBL self-assembly of branched PEI and PAA with the addition of $CaCl_2$ and nanoclay could mimic the strong structure of cephalopods and erase the surface scratches in 10 s. Especially, the existence of nanoclay led to the high water-holding capacity, repelled the colliding bubbles in wet state, and improved the oxygen barrier property to less than 1/100 of that of bare polyethylene.

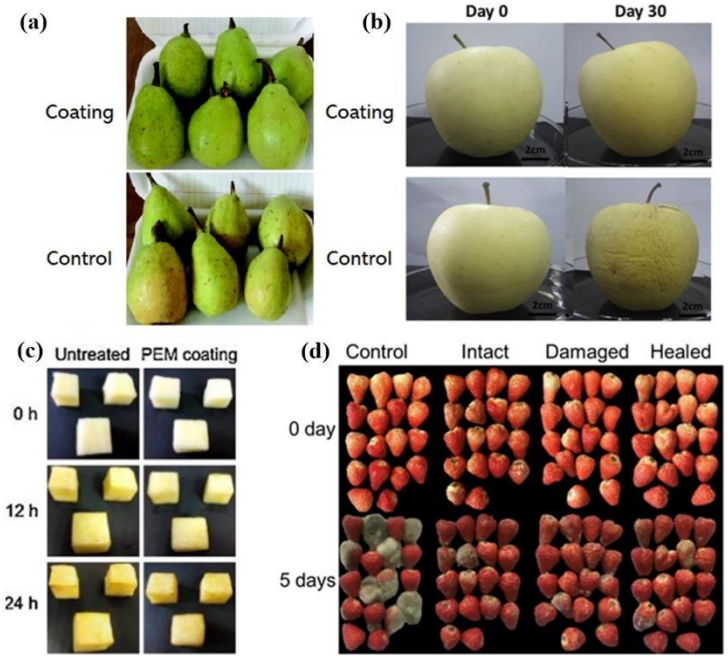


Figure 3. Applications of self-healing coatings in (a) pear, (b) apple, (c) apple slice, and (d) strawberry.[14,102,103,114]

Antimicrobial compounds can also be incorporated in self-healing coatings. Yang et al.[115] grafted l-menthol-β-CD with chitosan and assembled them with SA to form an edible coating. The self-healing ability was enabled by the synergistic effects of hydrogen bonds and host-guest reaction. The coating of 10 assembled layers had the transparency of 94% and the 63% recovery rate of the tensile strength (15.89 MPa) after 20 min self-healing process. Besides, the controlled release of l-menthol inhibited the growth of microorganisms and maintained the firmness of packaged apples, extending their shelf life to up to 30 days. Another self-healing coating with excellent antimicrobial activity was prepared from MoS_2 nanosheets, β-CD-modified PEI, and AD-modified PAA using the LBL self-assembly technique via host-guest interaction.[105] This coating showed a hydrophobic surface with a water contact angle of 98.02° and could self-heal within 30 min when exposed in a humid environment. The coating greatly suppressed the bacteria adhesion and inhibited the growth of *E. coli* and could even measure the concentration of Co^{2+} using fluorescence signal to prevent from consuming excessive heavy metals.

Similar to self-healing films, the fabrication of self-healing coatings with hydrophilic surfaces was applied as anti-fogging packaging materials. For instance, Yang et al.[116]

manufactured a high-transparency (> 95%) self-healing coating from (methacryloyloxy)ethyldimethyl-(3-sulfopropyl) (SBMA) and itaconic acid (IA). The self-healing process finished in 6 h at 25 ℃ and 55% RH and was due to the reconstruction of hydrogen bonds in the damaged area. Water droplets could be spread on the surface of the coating in 6 s with a contact angle of less than 10 ℃, and the coated glass slide was still transparent after being taken from the refrigerator to room temperature. Another anti-fogging coating was formed with pectin and TA and then applied to the surface of PET film.[108] The abundant -OH groups promoted the diffusion of water droplets, resulting in the excellent anti-fogging capability in both hot-vapor and cold-warm conditions. Moreover, the damaged coating could self-heal in 4 min and was well-retained after rinsing 5 times with a high-speed water faucet, indicating its durability and stability. Xu et al.[117] fabricated a robust and transparent (about 90%) self-healing coating from PVA, SA, TiO_2 and glycerin. The cross-linked coating had a water contact angle of 66.8° and was able to absorb the surrounding water vapor quickly, achieving the anti-fogging performance. Besides, after 100 cycles of abrasion by sandpaper at 25 Pa, the coating showed restorable antifogging performance after 1 second of water immersion or 5 minutes of solar irradiation treatment, due to the restoration of hydrogen bonds between the absorbed water molecules and the hydroxyl or carboxyl groups of PVA and SA.

4 Conclusions and outlook

Recent studies have reported the fabrication of self-healing materials through dynamic non-covalent interactions, dynamic covalent interactions, or their synergistic effects. Several attempts have been made to apply self-healing materials in food packaging in the forms of films or coatings with recoverable mechanical and barrier properties to better protect the packaged food products. Other functionalities such as antimicrobial and anti-fogging properties can also be incorporated to make the food packaging materials versatile. The applications of self-healing materials in food packaging are promising, but future research is required in the following areas:

1. The self-healing efficiency should be evaluated under different conditions (pH, temperature, humidity, etc.), especially the transportation and storage conditions of food products. Some self-healing processes require external stimuli such as high temperature or high humidity, which may not be suitable for food packaging.
2. The feasibility of self-healing materials should be considered. The packaging materials with high self-healing efficiency and good mechanical and gas barrier properties are absolutely preferred, but they should also be cost effective and nontoxic, and should not affect the texture and flavor of food products. Compared to the materials that need external stimuli to heal, the intrinsic self-healing films and coatings are more applicable.
3. Besides the toxicity, the migration of self-healing packaging materials should be carefully evaluated. Chemical modifications are commonly applied during the preparation of self-healing materials, so their fate in human body should be investigated. Moreover, the deterioration of food quality and nutritional value with the application of novel packaging materials should be studied case by case.
4. The post-consumer waste management of self-healing packaging materials should be investigated. The degradability of materials may be affected by physical/chemical modifications. Therefore, the degradation rate and products of self-healing materials under various conditions should be assessed.

Conflict of interest statement

Nothing declared.

Acknowledgements

Funding: This work was supported by the FRQNT– Projet de recherche en équipe [2021-PR-283095]; Natural Sciences and Engineering Research Council Discovery Grants [NSERC RGPIN-2019-04498]; and Natural Sciences and Engineering Research Council Discovery Launch Supplement [NSERC DGECR-2019-00472].

References

1. Gadwal I. A brief overview on preparation of self-healing polymers and coatings via hydrogen bonding interactions. *Macromol*. 2020; **1**(1): 18-36.
2. Ouarga A, Lebaz N, Tarhini M, Noukrati H, Barroug A, Elaissari A. Towards smart self-healing coatings: Advances in micro/nano-encapsulation processes as carriers for anti-corrosion coatings development. *J Mol Liq*. 2022: 118862.
3. Jafarzadeh S, Jafari SM. Impact of metal nanoparticles on the mechanical, barrier, optical and thermal properties of biodegradable food packaging materials. *Critical reviews in food science and nutrition*. 2021; **61**(16): 2640-2658.
4. Zhang P, Dai Y, Wang W, et al. Effects of magnesia expansive agents on the self-healing performance of microcracks in strain-hardening cement-based composites (SHCC). *Materials Today Communications*. 2020; **25**: 101421.
5. Cremaldi JC, Bhushan B. Bioinspired self-healing materials: lessons from nature. *Beilstein Journal of Nanotechnology*. 2018; **9**(1): 907-935.
6. Ji X, Li Z, Hu Y, et al. Bioinspired hydrogels with muscle-like structure for AIEgen-guided selective self-healing. *CCS Chemistry*. 2021; **3**(4): 1146-1156.
7. Zhong Y, Li P, Hao J, Wang X. Bioinspired self-healing of kinetically inert hydrogels mediated by chemical nutrient supply. *ACS Applied Materials & Interfaces*. 2020; **12**(5): 6471-6478.
8. Brinkman E. Self healing materials concept and applications. *Betase BV IOP*. 2011; **100**(47): 5424-30.
9. Malinskii YM, Prokopenko V, Ivanova N, Kargin V. Investigation of self-healing of cracks in polymers. *Polymer Mechanics*. 1970; **6**(2): 240-244.
10. Van Der Zwaag S. Self-healing materials: an alternative approach to 20 centuries of material science. *Delft: Springer*. 2007:
11. Multanen V, Bhushan B. Bioinspired self-healing, superliquiphobic and self-cleaning hydrogel-coated surfaces with high durability. *Philosophical Transactions of the Royal Society A*. 2019; **377**(2150): 20190117.
12. Liu X, Yang K, Chang M, Wang X, Ren J. Fabrication of cellulose nanocrystal reinforced nanocomposite hydrogel with self-healing properties. *Carbohydr Polym*. 2020; **240**: 116289.
13. Xiao L, Shi J, Wu K, Lu M. Self-healing supramolecular waterborne polyurethane based on host–guest interactions and multiple hydrogen bonds. *React Funct Polym*. 2020; **148**: 104482.
14. Du Y, Yang F, Yu H, et al. Fabrication of novel self-healing edible coating for fruits preservation and its performance maintenance mechanism. *Food Chem*. 2021; **351**: 129284.
15. Li L, Yan B, Yang J, Huang W, Chen L, Zeng H. Injectable self-healing hydrogel with antimicrobial and antifouling properties. *ACS applied materials & interfaces*. 2017; **9**(11): 9221-9225.
16. Xu C, Zhan W, Tang X, Mo F, Fu L, Lin B. Self-healing chitosan/vanillin hydrogels based on Schiff-base bond/hydrogen bond hybrid linkages. *Polym Test*. 2018; **66**: 155-163.
17. Chen D, Chang L, Zhou Z, et al. Pectin-based self-healing hydrogel with NaHCO3 degradability for drug loading and release. *Journal of Polymer Research*. 2021; **28**(2):

1-10.
18. Li D-q, Wang S-y, Meng Y-j, Guo Z-w, Cheng M-m, Li J. Fabrication of self-healing pectin/chitosan hybrid hydrogel via Diels-Alder reactions for drug delivery with high swelling property, pH-responsiveness, and cytocompatibility. *Carbohydr Polym*. 2021; **268**: 118244.
19. Fang Y, Du X, Jiang Y, et al. Thermal-driven self-healing and recyclable waterborne polyurethane films based on reversible covalent interaction. *ACS Sustainable Chemistry & Engineering*. 2018; **6**(11): 14490-14500.
20. Huang K, Yuan Y, Baojun X. A Critical Review on the Microencapsulation of Bioactive Compounds and Their Application. *Food Rev Int*. 2021: 1-41.
21. Wang X, Yin H, Chen Z, Xia L. Epoxy resin/ethyl cellulose microcapsules prepared by solvent evaporation for repairing microcracks: Particle properties and slow-release performance. *Materials Today Communications*. 2020; **22**: 100854.
22. Lu T, Li B, Sun D, Hu M, Ma J, Sun G. Advances in controlled release of microcapsules and promising applications in self-healing of asphalt materials. *Journal of Cleaner Production*. 2021; **294**: 126270.
23. Yeo YH, Park WH. Dual-crosslinked, self-healing and thermo-responsive methylcellulose/chitosan oligomer copolymer hydrogels. *Carbohydr Polym*. 2021; **258**: 117705.
24. Zhu J, Wu Y, Huang X, et al. Self-healing liquid metal nanoparticles encapsulated in hollow carbon fibers as a free-standing anode for lithium-ion batteries. *Nano Energy*. 2019; **62**: 883-889.
25. Su J-F, Zhang X-L, Guo Y-D, et al. Experimental observation of the vascular self-healing hollow fibers containing rejuvenator states in bitumen. *Construction and Building Materials*. 2019; **201**: 715-727.
26. Yang J, Shen M, Luo Y, et al. Advanced applications of chitosan-based hydrogels: From biosensors to intelligent food packaging system. *Trends Food Sci Technol*. 2021; **110**: 822-832.
27. Liu Q, Ji N, Xiong L, Sun Q. Rapid gelling, self-healing, and fluorescence-responsive chitosan hydrogels formed by dynamic covalent crosslinking. *Carbohydrate Polymers*. 2020; **246**: 116586.
28. Yang Y, Ren J, Luo C, Yuan R, Ge L. Fabrication of l-menthol contained edible self-healing coating based on guest-host interaction. *Colloids Surf Physicochem Eng Aspects*. 2020; **597**: 124743.
29. Hu B, Chen L, Lan S, et al. Layer-by-layer assembly of polysaccharide films with self-healing and antifogging properties for food packaging applications. *ACS Applied Nano Materials*. 2018; **1**(7): 3733-3740.
30. Choi S, Eom Y, Kim SM, et al. A self-healing nanofiber-based self-responsive time-temperature indicator for securing a cold-supply chain. *Adv Mater*. 2020; **32**(11): 1907064.
31. Liu X, Han W, Zhu Y, et al. Anti-oxidative and antibacterial self-healing edible polyelectrolyte multilayer film in fresh-cut fruits. *Journal of Nanoscience and*

Nanotechnology. 2018; **18**(4): 2592-2600.
32. Zhang C, Wang H, Zhou Q. Preparation and characterization of microcapsules based self-healing coatings containing epoxy ester as healing agent. *Prog Org Coat*. 2018; **125**: 403-410.
33. Rao J, Liu N, Zhang Z, et al. All-fiber-based quasi-solid-state lithium-ion battery towards wearable electronic devices with outstanding flexibility and self-healing ability. *Nano Energy*. 2018; **51**: 425-433.
34. Cai G, Wang J, Qian K, Chen J, Li S, Lee PS. Extremely stretchable strain sensors based on conductive self-healing dynamic cross-links hydrogels for human-motion detection. *Advanced Science*. 2017; **4**(2): 1600190.
35. Ding C, Tian M, Feng R, Dang Y, Zhang M. Novel self-healing hydrogel with injectable, pH-responsive, strain-sensitive, promoting wound-healing, and hemostatic properties based on collagen and chitosan. *ACS Biomaterials Science & Engineering*. 2020; **6**(7): 3855-3867.
36. Huang S, Wan F, Bi S, Zhu J, Niu Z, Chen J. A self-healing integrated all-in-one zinc-ion battery. *Angew Chem*. 2019; **131**(13): 4357-4361.
37. Althaqafi KA, Satterthwaite J, Silikas N. A review and current state of autonomic self-healing microcapsules-based dental resin composites. *Dent Mater*. 2020; **36**(3): 329-342.
38. Zhu Y, Cao K, Chen M, Wu L. Synthesis of UV-responsive self-healing microcapsules and their potential application in aerospace coatings. *ACS applied materials & interfaces*. 2019; **11**(36): 33314-33322.
39. Szabó T, Molnár-Nagy L, Bognár J, Nyikos L, Telegdi J. Self-healing microcapsules and slow release microspheres in paints. *Prog Org Coat*. 2011; **72**(1-2): 52-57.
40. Li Q, Liu C, Wen J, Wu Y, Shan Y, Liao J. The design, mechanism and biomedical application of self-healing hydrogels. *Chinese Chemical Letters*. 2017; **28**(9): 1857-1874.
41. Batista RA, Espitia PJP, Quintans JdSS, et al. Hydrogel as an alternative structure for food packaging systems. *Carbohydr Polym*. 2019; **205**: 106-116.
42. Bei Y, Ma Y, Song F, et al. Recent progress of biomass based self-healing polymers. *J Appl Polym Sci*. 2022; **139**(16): 51977.
43. Formoso E, Asua JM, Matxain JM, Ruipérez F. The role of non-covalent interactions in the self-healing mechanism of disulfide-based polymers. *Physical Chemistry Chemical Physics*. 2017; **19**(28): 18461-18470.
44. Wang W, Zhang Y, Liu W. Bioinspired fabrication of high strength hydrogels from non-covalent interactions. *Prog Polym Sci*. 2017; **71**: 1-25.
45. Liu J-D, Du X-Y, Wang C-F, Li Q, Chen S. Construction of triple non-covalent interaction-based ultra-strong self-healing polymeric gels via frontal polymerization. *Journal of Materials Chemistry C*. 2020; **8**(40): 14083-14091.

46. Sharma S, Kumar A, Kumar R, Rana NK, Koch B. Development of a novel chitosan based biocompatible and self-healing hydrogel for controlled release of hydrophilic drug. *Int J Biol Macromol*. 2018; **116**: 37-44.
47. Lin Q, Li H, Ji N, Dai L, Xiong L, Sun Q. Self-healing, stretchable, and freezing-resistant hydroxypropyl starch-based double-network hydrogels. *Carbohydr Polym*. 2021; **251**: 116982.
48. Fan Z, Duan L, Gao G. Self-healing carrageenan-driven Polyacrylamide hydrogels for strain sensing. *Science China Technological Sciences*. 2020; **63**(12): 2677-2686.
49. Kim JR, Netravali AN. Self-healing green composites based on soy protein and microfibrillated cellulose. *Composites Science and Technology*. 2017; **143**: 22-30.
50. Ghorpade VS, Dias RJ, Mali KK, Mulla SI. Citric acid crosslinked carboxymethylcellulose-polyvinyl alcohol hydrogel films for extended release of water soluble basic drugs. *J Drug Deliv Sci Technol*. 2019; **52**: 421-430.
51. Su Y, Wu Y, Liu M, Qing Y, Zhou J, Wu Y. Ferric Ions Modified Polyvinyl Alcohol for Enhanced Molecular Structure and Mechanical Performance. *Materials*. 2020; **13**(6): 1412.
52. Pan J, Jin Y, Lai S, Shi L, Fan W, Shen Y. An antibacterial hydrogel with desirable mechanical, self-healing and recyclable properties based on triple-physical crosslinking. *Chemical Engineering Journal*. 2019; **370**: 1228-1238.
53. Liu T, Zou S, Hang C, et al. Mechanically strong and tough hydrogels with pH-triggered self-healing and shape memory properties based on a dual physically crosslinked network. *Polymer Chemistry*. 2020; **11**(11): 1906-1918.
54. Zhu X, Zheng W, Zhao H, Wang L. Non-covalent assembly of a super-tough, highly stretchable and environmentally adaptable self-healing material inspired by nacre. *Journal of Materials Chemistry A*. 2021; **9**(36): 20737-20747.
55. Qiao L, Liu C, Liu C, et al. Self-healing alginate hydrogel based on dynamic acylhydrazone and multiple hydrogen bonds. *Journal of Materials Science*. 2019; **54**(11): 8814-8828.
56. Qiao L, Liu C, Liu C, et al. Self-healing, pH-sensitive and shape memory hydrogels based on acylhydrazone and hydrogen bonds. *Eur Polym J*. 2022; **162**: 110838.
57. Liu J, Zhou Z, Su X, Cao J, Chen M, Liu R. Stiff UV-Curable self-healing coating based on double reversible networks containing diels-alder cross-linking and hydrogen bonds. *Prog Org Coat*. 2020; **146**: 105699.
58. Schäfer S, Kickelbick G. Double reversible networks: improvement of self-healing in hybrid materials via combination of diels–alder cross-linking and hydrogen bonds. *Macromolecules*. 2018; **51**(15): 6099-6110.
59. Wang W, Narain R, Zeng H. Rational design of self-healing tough hydrogels: a mini review. *Frontiers in chemistry*. 2018: 497.
60. Tang L, Liao S, Qu J. Self-healing and multistimuli-responsive hydrogels formed via a cooperation strategy and their application in detecting biogenic amines. *ACS applied materials & interfaces*. 2018; **10**(32): 27365-27373.
61. Zhou Q, Dong X, Xiong Y, et al. Multi-responsive lanthanide-based hydrogel with encryption, naked eye sensing, shape memory, self-healing, and antibacterial activity. *ACS Applied Materials & Interfaces*. 2020; **12**(25): 28539-28549.

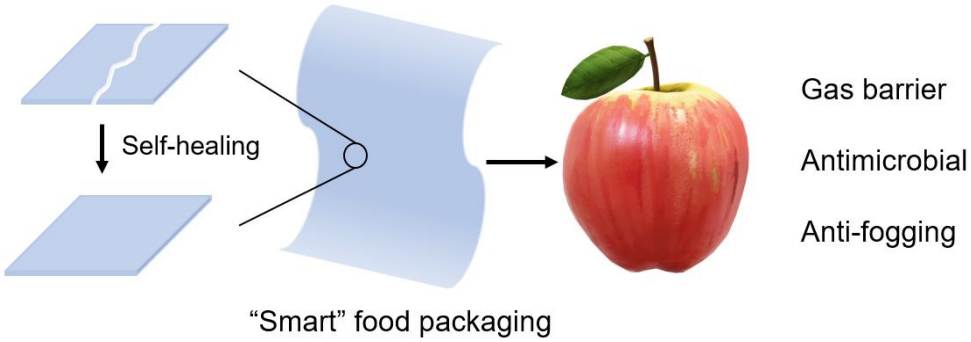
62. Zheng Q, Zhao L, Wang J, Wang S, Liu Y, Liu X. High-strength and high-toughness sodium alginate/polyacrylamide double physically crosslinked network hydrogel with superior self-healing and self-recovery properties prepared by a one-pot method. *Colloids Surf Physicochem Eng Aspects*. 2020; **589**: 124402.
63. Deng Y, Huang M, Sun D, et al. Dual physically cross-linked κ-carrageenan-based double network hydrogels with superior self-healing performance for biomedical application. *ACS applied materials & interfaces*. 2018; **10**(43): 37544-37554.
64. Yuan T, Cui X, Liu X, Qu X, Sun J. Highly tough, stretchable, self-healing, and recyclable hydrogels reinforced by in situ-formed polyelectrolyte complex nanoparticles. *Macromolecules*. 2019; **52**(8): 3141-3149.
65. Zhang Y, Hu Q, Yang S, Wang T, Sun W, Tong Z. Unique Self-Reinforcing and Rapid Self-Healing Polyampholyte Hydrogels with a pH-Induced Shape Memory Effect. *Macromolecules*. 2021; **54**(11): 5218-5228.
66. Lin Y, Zeng Z, Li Y, et al. Self-healing zwitterionic sulfobetaine nanocomposite hydrogels with good mechanical properties. *RSC advances*. 2019; **9**(55): 31806-31811.
67. Zhao J, Xi X, Ouyang H, et al. Acidic and alkaline gas sensitive and self-healing chitosan aerogel based on electrostatic interaction. *Carbohydr Polym*. 2021; **272**: 118445.
68. Hao X, Wang W, Yang Z, et al. pH responsive antifouling and antibacterial multilayer films with Self-healing performance. *Chem Eng J*. 2019; **356**: 130-141.
69. Yang J, Yi L, Fang X, et al. Self-healing and recyclable biomass aerogel formed by electrostatic interaction. *Chem Eng J*. 2019; **371**: 213-221.
70. Maiz-Fernández S, Barroso N, Pérez-Álvarez L, Silván U, Vilas-Vilela JL, Lanceros-Mendez S. 3D printable self-healing hyaluronic acid/chitosan polycomplex hydrogels with drug release capability. *Int J Biol Macromol*. 2021; **188**: 820-832.
71. Fan X, Wang T, Miao W. The preparation of pH-sensitive hydrogel based on host-guest and electrostatic interactions and its drug release studies in vitro. *Journal of Polymer Research*. 2018; **25**(10): 1-10.
72. Li Z, Yu R, Guo B. Shape-Memory and Self-Healing Polymers Based on Dynamic Covalent Bonds and Dynamic Noncovalent Interactions: Synthesis, Mechanism, and Application. *ACS Applied Bio Materials*. 2021; **4**(8): 5926-5943.
73. Mohamadhoseini M, Mohamadnia Z. Supramolecular self-healing materials via host-guest strategy between cyclodextrin and specific types of guest molecules. *Coord Chem Rev*. 2021; **432**: 213711.
74. Peng L, Lin M, Zhang S, Li L, Fu Q, Hou J. A self-healing coating with UV-shielding property. *Coatings*. 2019; **9**(7): 421.
75. Mohamadhoseini M, Mohamadnia Z. Alginate-based self-healing hydrogels assembled by dual cross-linking strategy: Fabrication and evaluation of mechanical properties. *Int J Biol Macromol*. 2021; **191**: 139-151.
76. Xuan H, Ren J, Zhang J, Ge L. Novel highly-flexible, acid-resistant and self-healing host-guest transparent multilayer films. *Appl Surf Sci*. 2017; **411**: 303-314.
77. Mo C, Xiang L, Chen Y. Advances in Injectable and Self-healing Polysaccharide Hydrogel Based on the Schiff Base Reaction. *Macromol Rapid Commun*. 2021; **42**(10):

2100025.
78. Pettignano A, Häring M, Bernardi L, Tanchoux N, Quignard F, Díaz DD. Self-healing alginate–gelatin biohydrogels based on dynamic covalent chemistry: elucidation of key parameters. *Materials Chemistry Frontiers*. 2017; **1**(1): 73-79.
79. Yang X, Li P, Tang W, et al. A facile injectable carbon dot/oxidative polysaccharide hydrogel with potent self-healing and high antibacterial activity. *Carbohydr Polym*. 2021; **251**: 117040.
80. Wang W, Xiang L, Gong L, et al. Injectable, self-healing hydrogel with tunable optical, mechanical, and antimicrobial properties. *Chem Mater*. 2019; **31**(7): 2366-2376.
81. Xiao G, Wang Y, Zhang H, Chen L, Fu S. Facile strategy to construct a self-healing and biocompatible cellulose nanocomposite hydrogel via reversible acylhydrazone. *Carbohydr Polym*. 2019; **218**: 68-77.
82. Dahlke J, Zechel S, Hager MD, Schubert US. How to design a self-healing polymer: general concepts of dynamic covalent bonds and their application for intrinsic healable materials. *Advanced Materials Interfaces*. 2018; **5**(17): 1800051.
83. Huang K, Xu H, Chen C, et al. A novel dual crosslinked polysaccharide hydrogel with self-healing and stretchable properties. *Polymer Chemistry*. 2021; **12**(42): 6134-6144.
84. Zhu M, Jin H, Shao T, et al. Polysaccharide-based fast self-healing ion gel based on acylhydrazone and metal coordination bonds. *Materials & Design*. 2020; **192**: 108723.
85. Zhang L, Michel Jr FC, Co AC. Nonisocyanate route to 2, 5-bis (hydroxymethyl) furan-based polyurethanes crosslinked by reversible diels–alder reactions. *J Polym Sci, Part A: Polym Chem*. 2019; **57**(14): 1495-1499.
86. Buono P, Duval A, Averous L, Habibi Y. Thermally healable and remendable lignin-based materials through Diels–Alder click polymerization. *Polymer*. 2017; **133**: 78-88.
87. Ye J, Fu S, Zhou S, et al. Advances in hydrogels based on dynamic covalent bonding and prospects for its biomedical application. *Eur Polym J*. 2020; **139**: 110024.
88. Cai S, Qiang Z, Zeng C, Ren J. Multifunctional poly (lactic acid) copolymers with room temperature self-healing and rewritable shape memory properties via Diels-Alder reaction. *Materials Research Express*. 2019; **6**(4): 045701.
89. Perera MM, Ayres N. Dynamic covalent bonds in self-healing, shape memory, and controllable stiffness hydrogels. *Polymer Chemistry*. 2020; **11**(8): 1410-1423.
90. Jian X, Hu Y, Zhou W, Xiao L. Self-healing polyurethane based on disulfide bond and hydrogen bond. *Polym Adv Technol*. 2018; **29**(1): 463-469.
91. Du J, Choi B, Liu Y, Feng A, Thang SH. Degradable pH and redox dual responsive nanoparticles for efficient covalent drug delivery. *Polymer Chemistry*. 2019; **10**(11): 1291-1298.
92. Chang K, Jia H, Gu S-Y. A transparent, highly stretchable, self-healing

polyurethane based on disulfide bonds. *Eur Polym J*. 2019; **112**: 822-831.
93. Xia T, Jiang X, Deng L, Yang M, Chen X. Albumin-based dynamic double cross-linked hydrogel with self-healing property for antimicrobial application. *Colloids Surf B Biointerfaces*. 2021; **208**: 112042.
94. Wang Y, Xiao G, Peng Y, Chen L, Fu S. Effects of cellulose nanofibrils on dialdehyde carboxymethyl cellulose based dual responsive self-healing hydrogel. *Cellulose*. 2019; **26**(16): 8813-8827.
95. Mredha MTI, Na JY, Seon J-K, Cui J, Jeon I. Multifunctional poly (disulfide) hydrogels with extremely fast self-healing ability and degradability. *Chem Eng J*. 2020; **394**: 124941.
96. Mlalila N, Kadam DM, Swai H, Hilonga A. Transformation of food packaging from passive to innovative via nanotechnology: concepts and critiques. *J Food Sci Technol*. 2016; **53**(9): 3395-3407.
97. Smirnov MA, Nikolaeva AL, Bobrova NV, et al. Self-healing films based on chitosan containing citric acid/choline chloride deep eutectic solvent. *Polym Test*. 2021; **97**: 107156.
98. Ouyang Z, Yu H-Y, Song M, Zhu J, Wang D. Ultrasensitive and robust self-healing composite films with reinforcement of multi-branched cellulose nanocrystals. *Composites Science and Technology*. 2020; **198**: 108300.
99. Xuan H, Zhu Y, Ren J, Dai W, Ge L. Self-healing, antibacterial, and dual cross-linked multilayer films for microcapsule-based controllable drug release applications. *Appl Surf Sci*. 2019; **476**: 182-188.
100. Song Y, Meyers KP, Gerringer J, et al. Fast Self-Healing of Polyelectrolyte Multilayer Nanocoating and Restoration of Super Oxygen Barrier. *Macromol Rapid Commun*. 2017; **38**(10): 1700064.
101. Wang Y, Yao L, Ren T, He J. Robust yet self-healing antifogging/antibacterial dual-functional composite films by a simple one-pot strategy. *Journal of colloid and interface science*. 2019; **540**: 107-114.
102. Sultan M, Hafez OM, Saleh MA, Youssef AM. Smart edible coating films based on chitosan and beeswax–pollen grains for the postharvest preservation of Le Conte pear. *RSC Advances*. 2021; **11**(16): 9572-9585.
103. Manabe K, Koyama E, Norikane Y. Cephalopods-Inspired Rapid Self-Healing Nanoclay Composite Coatings with Oxygen Barrier and Super-Bubble-Phobic Properties. *ACS Applied Materials & Interfaces*. 2021; **13**(30): 36341-36349.
104. Xuan H, Zhu Y, Ren J, Ge L. Intrinsic self-healing and biocompatibility of carbon nitride coatings via inhibiting or degrading ethylene for fruit preservation. *Journal of Materials Science*. 2019; **54**(12): 9282-9290.
105. Xuan H, Dai W, Zhu Y, Ren J, Zhang J, Ge L. Self-Healing, antibacterial and sensing nanoparticle coating and its excellent optical applications. *Sensors Actuators B: Chem*. 2018; **257**: 1110-1117.
106. Zhao Z, Xie H, Yang D, et al. A nanosheets-polyborosiloxane composite impregnated with shorter hydrogen-bonding clusters achieves combination of self-healing, shapeability and high-barrier properties. *Polymer*. 2022: 125013.

107. Mou K, Li J, Wang Y, Cha R, Jiang X. 2, 3-Dialdehyde nanofibrillated cellulose as a potential material for the treatment of MRSA infection. *Journal of Materials Chemistry B*. 2017; **5**(38): 7876-7884.
108. Zhang T, Fang L, Lin N, et al. Highly transparent, healable, and durable anti-fogging coating by combining hydrophilic pectin and tannic acid with poly (ethylene terephthalate). *Green Chem*. 2019; **21**(19): 5405-5413.
109. Saddique A, Lee HM, Kim JC, Bae J, Cheong IW. Cellulose nanocrystal nanocomposites capable of low-temperature and fast self-healing performance. *Carbohydr Polym*. 2022; **296**: 119973.
110. Zhu M, Ying D, Zhang H, Xu X, Chang C. Self-healable hydrophobic films fabricated by incorporating natural wax into cellulose matrix. *Chem Eng J*. 2022; **446**: 136791.
111. Li F, Ye Q, Gao Q, et al. Facile fabrication of self-healable and antibacterial soy protein-based films with high mechanical strength. *ACS applied materials & interfaces*. 2019; **11**(17): 16107-16116.
112. Chang Z, Zhang S, Li F, et al. Self-healable and biodegradable soy protein-based protective functional film with low cytotoxicity and high mechanical strength. *Chem Eng J*. 2021; **404**: 126505.
113. Chen X-C, Huang W-P, Ren K-F, Ji J. Self-healing label materials based on photo-cross-linkable polymeric films with dynamic surface structures. *Acs Nano*. 2018; **12**(8): 8686-8696.
114. Liu X, Tang C, Han W, et al. Characterization and preservation effect of polyelectrolyte multilayer coating fabricated by carboxymethyl cellulose and chitosan. *Colloids Surf Physicochem Eng Aspects*. 2017; **529**: 1016-1023.
115. Sultan M, Hafez OM, Saleh MA. Quality assessment of lemon (Citrus aurantifolia, swingle) coated with self-healed multilayer films based on chitosan/carboxymethyl cellulose under cold storage conditions. *Int J Biol Macromol*. 2022; **200**: 12-24.
116. Yang H, Jin K, Wang H, et al. Facile preparation of a high-transparency zwitterionic anti-fogging poly (SBMA-co-IA) coating with self-healing property. *Prog Org Coat*. 2022; **165**: 106764.
117. Xu X, Zhu T, Zheng W, et al. A robust and transparent hydrogel coating for sustainable antifogging with excellent self-cleaning and self-healing ability. *Chem Eng J*. 2023; **451**: 137879.

Graphical Table of Contents



This review highlights a promising approach to combat damage to food packaging materials during transportation, handling, and storage. We summarized the recent progress in the preparation of self-healing materials through different mechanisms, compared the self-healing efficiency under different conditions, highlighted the potential applications of self-healing films and coatings with recoverable mechanical and barrier properties and other functionalities (e.g. antimicrobial and anti-fogging capacities), and discussed their future opportunities, challenges and research directions.