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Self-healing Polyelectrolyte Multilayer Composite Film with Microcapsules

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Abstract: Self-healing materials are gradually developing because they can restore structural properties and maintain their function after being damaged. Here, branched poly (ethyleneimine) (bPEI), poly (acrylic acid) (PAA) and microcapsules were used to fabricate the functional (bPEI/PAA)*30-microcapsules composite PEM film based on layer-by-layer (LbL) self-assembly technique. As a proof of concept, model molecules, hydrophilic rhodamine B (RB) and hydrophobic Roxithromycin (ROX), were loaded in the (bPEI/PAA)*30-microcapsules composite PEM film to prove that microcapsules is a promising candidate as functional carrier to endow self-healing film with the desired functional properties. The results indicate that the microcapsules can be assembled successfully on the polyelectrolyte multilayer (PEM) film, the as-prepared (bPEI/PAA)*30-microcapsules composite PEM film can not only be tailored with desired property but also show excellent self-healing ability. According to our study, much more functional molecules can be grafted onto self-healing PEM film through microcapsules and the prepared functional self-healing PEM composite film will have great potential applications in the future.

Keywords: LbL; microcapsules; self-healing; composite film; functional

1 Introduction

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When accidentally injured, such as cuts or bruises on skin, the wound can slowly heal itself. Inspired by this amazing phenomenon, scientists begin to study and design new materials with self-healing property like skin. Self-healing polymer materials are expected to contribute greatly to the safety and durability of polymeric components without the high costs of external repair, and they offer great opportunities for broadening the applications of polymer materials.[1] In general, self-healing polymers can be grouped into two categories.[2] Extrinsic self-healing materials,[3] including capsule-based healing systems and vascular healing systems, utilize healing agents captured or encapsulated in hollow fibers, microspheres and other containers;[4] intrinsic self-healing materials based on either covalent interactions,[5] such as Diels–Alder (DA) and retro Diels–Alder (RDA) processes,[6] or non-covalent interactions such as hydrogen bonding,[7] ionic interactions,[8] π-π interactions,[9] host-guest interactions, metal-ligand coordination,[10] and supramolecular interaction.[11] As extrinsic self-healing materials require the healing agents and cannot repeated repair, intrinsic self-healing materials which can endlessly heal themselves have received more and more research interests.

Through efforts of researchers, self-healing materials are gradually moving from restoring mechanical and structural properties to healing of functions. Although there have been some achievements about self-healing polymers and polymer composites for functional applications,[12-15] like self-healing hydrogels that promise a bright prospect in drug release and tissue engineering,[16] these properties are potential candidates of materials itself and have some limitations in application. Technically, integration of self-healable multifunctionality into single materials might be hard to achieve. So, some researchers try to graft versatile functional material systems on the self-healing materials to obtain the desired functions. For instance, self-healing

polymers deposited with good conductive materials such as Ag nanowires, carbon nanotubes (CNTs) or graphene for high-energy lithium-ion batteries,[17] supercapacitor,[18] electrically conducting wires, wearable microelectronics[19] and electronic skin applications.[20, 21] These works all focus on grafting the materials or molecules which possess specific features on self-healing materials, if the desired "functional carrier" rather than specific material can be grafted on to intrinsic self-healing materials, the process of the functional self-healing materials will be promoted more efficiently and be simplified to a large extent. The application of functional self-healing materials will be greatly broaden. Junqi Sun ever assembled drug loaded micelles into bPEI/PAA self-healing films to solve the problem of hydrophobic molecules are difficult to incorporate directly into LbL-assembled films.[22] The author believe that microcapsule is a more suitable candidate for functional carrier as its composition, structural, physico-chemical and mechanical property can be tailored at nanometer scale,[23] its interior can be embedded with a variety of different materials, such as drugs, dyes, nano-particles and living cells,[24] and it can release them at the specific target by external stimuli.[25]

LbL self-assembly technique is a versatile approach to fabricate nanostructure thin films and is typically accomplished by alternating the adsorption of mutually interacting polymers on surfaces.[26, 27] The driving force to construct these films is non-covalent intermolecular interactions among charged or hydrogen-bonding moieties.[28] Nowadays, many studies have focused on the LbL self-assembly technique as a new approach to produce multilayered self-healing films.[27, 29-33] In our previous work,[34] graphene improved electrochemical property in self-healing PEM film also be successfully synthesized by this method.

Frequent contact with fingers can leave behind infectious bacteria and viruses on the surface of public facilities and medical devices, which are then readily transferred to people who touch them, leaving a severe threat to human health. Generally, the antibacterial surface coatings are prone to damage,[35] considering these facts, it is highly desirable to fabricate films that are antibacterial and capable of healing scratches for application in surface coatings of public devices.[22] In this paper, antibacterial self-healing PEM composite film was fabricated with functional carriers (microcapsules), bPEI and PAA based on LbL self-assembly technique. The obtained (bPEI/PAA)*30-microcapsules composite PEM film shows excellent self-healing ability and antibacterial property. What is more, other molecules can be easily loaded in (bPEI/PAA)*30-microcapsules composite PEM film and endow film with desired functional properties. It is promised to be greatly broaden the future applications of self-healing materials.

2. Experimental

2.1. Chemicals and materials

SiO_2 nanoparticles were achieved from Nanjing Dongjian Biological Technology Co. Ltd.; Ethanol, hydrofluoric acid, hydrogen peroxide, sulfuric acid and rhodamine B (RB) were obtained from Sinopharm Chemical Reagent Shanghai Co. Ltd.; Poly (sodium styrenesulfonate) (PSS, Mw≈70000), poly (allylamine hydrochloride) (PAH, Mw≈70000), poly (acrylic acid) (PAA, Mw≈1800, pH=3.0) and branched poly (ethyleneimine) (bPEI, Mw≈750000, pH=10.5) were obtained from Sigma-Aldrich Co. Ltd.; All reagents were used as received. Roxithromycin (ROX) was obtained from United Laboratories. The glass and quartz substrates were soaked in the mixture of 98% H_2SO_4/30% H_2O_2 (volumetric ratio 3:1) for 24 h, then, the glass and quartz

substrates were rinsed with ethyl alcohol and ultrapure water several times, and finally were dried with N_2 stream. In that order, the glass and quartz substrates were negatively charged after the treatments.

2.2. Preparation of the microcapsules

Multilayer microcapsules were accomplished by adsorption of positive charged PAH onto SiO_2 nanoparticles. Oppositely charged polyelectrolyte (PSS) was subsequently added to the suspension followed by repeated centrifugation. After the expected layers were absorbed, hydrofluoric acid solution (4%, v/v) was used to remove the core. PAH was used to form the first layer and the outmost layer. Some microcapsules were cooled to −20 °C and freeze-dried at this temperature for more than 2 days. The drug-loaded microcapsules were obtained by immersing the microcapsules in RB solution and ROX alcoholic solution for 24 h respectively. 2.3. Synthesis and preparation of the self-healing PEM films.

First, the prepared glass was immersed in bPEI solution for 15 min; then, the substrate was soaked in ultrapure water for 5 min to remove the bPEI that didn't adsorbed on substrate. Second, to obtain (bPEI/PAA)*1 film, the bPEI-substrate was immersed in PAA solution for 15 min, then the (bPEI/PAA)*1 film was soaked in ultrapure water for 5 min to remove the excess PAA. Repeated first and second processes 29 cycles, the (bPEI/PAA)*30 PEM film was obtained. Third, the (bPEI/PAA)*30 PEM film was immersed in microcapsules solution, after the sample was soaked in ultrapure water for 5 min to remove the excess microcapsules, the (bPEI/PAA)*30-microcapsules composite PEM film was obtained.

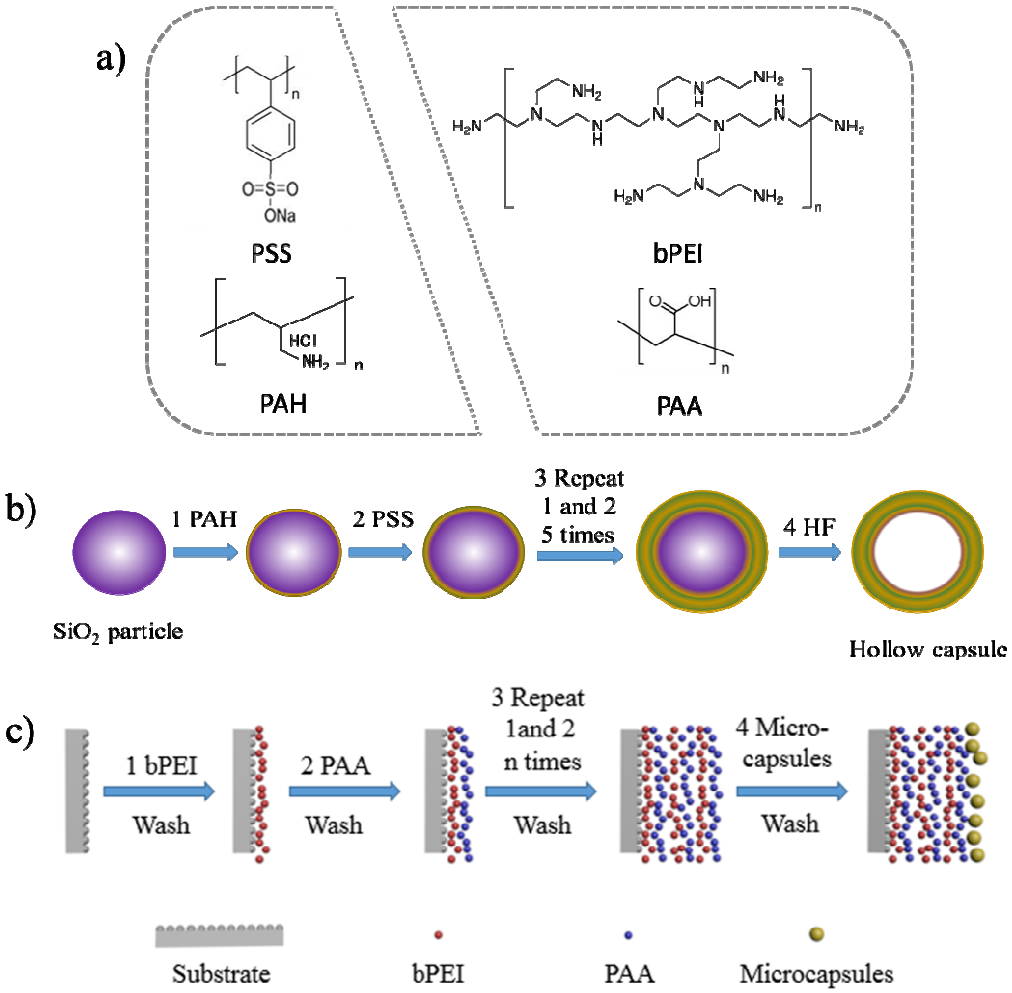

Fig. 1. (a) The chemical structures of PSS, PAH, bPEI and PAA, diagram of synthetic process of (b) the hollow microcapsules and (c) the (bPEI/PAA)*30-microcapsules PEM composite film.

2.4 Characterization

UV spectra of the prepared samples were obtained on U-4100 Spectrometer (HITACHI). The surface morphology of the prepared samples was characterized by field emission scanning electron microscopy (FESEM, Ultra Plus Zeiss). The water contact angle of the prepared samples was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shanghai Zhongchen Digital Technology Equipment Co., Ltd., Shanghai, China). The self-healing process and surface behavior

of the samples were observed by Stereo Microscope (MVX10 OLYMPUS). The mechanical properties of the samples were measured by Nano Test (Micro Materials)

3 Results and discussions

3.1. The composition, morphology and structure analysis

In this article, UV–VIS spectroscopy was used to monitor the presence of microcapsules in (bPEI/PAA)*30-microcapsules composite PEM film. Fig. 2 shows the results of (bPEI/PAA)*30 PEM film, (bPEI/PAA)*30-microcapsules composite PEM films and microcapsules on a quartz substrate. The absorption band around at 226 nm in (c) present the aromatic group in PSS polyanion. The absorbance at 270 nm corresponds to the crosslinking degree of the microcapsules[36] and can be regarded as another character of the microcapsules. The polycation PAH does not have absorption band above 200 nm, and its presence in the film does not contribute to the absorption spectra. Compared to the (bPEI/PAA)*30 PEM film, the two absorption bands at 225 and 270 nm can be easily found in (bPEI/PAA)*30-microcapsules composite PEM film while there is none in (bPEI/PAA)*30 PEM film. The UV–VIS spectroscopy shows a clear evidence that the microcapsules were successfully assembled on the (bPEI/PAA)*30-microcapsules composite PEM film.

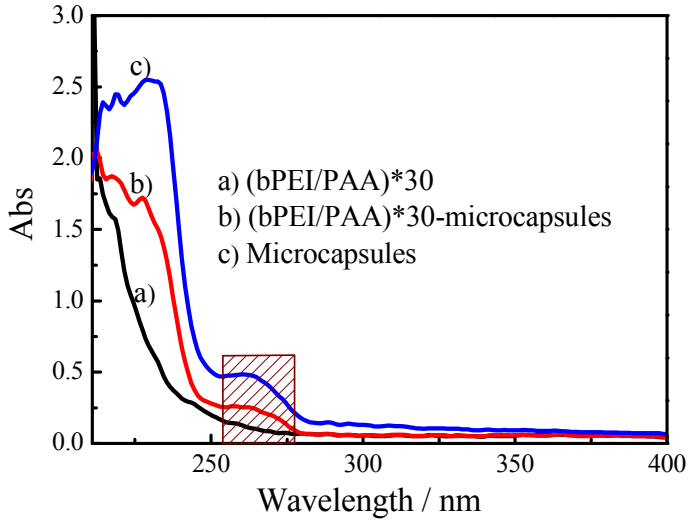

Fig. 2. UV spectra of (a) (bPEI/PAA)*30 PEM film, (b) (bPEI/PAA)*30-microcapsules composite PEM film and (c) microcapsules.

The FESEM images of microcapsules dried at room temperature, treated with the freeze-dried technique, (bPEI/PAA)*30 PEM film and (bPEI/PAA)*30-microcapsules composite PEM film dried at room temperature are shown in Fig. 3. When the samples were dried at room temperature, they collapsed because of the surface tension (a), indicating that the microcapsules have hollow morphology. From the (b) one can find that the microcapsules can maintain their structure and not collapse during dissolving out the template. This is because freeze-drying technique is based on the dehydration by sublimation of a frozen product, so that can maximum maintain the sample's real structure in the hydrated state.

Image (c) shows a relative smooth surface, but (d) presents a large difference from (c). There are massive of different spherical structures which adsorbing on the surface of the PEM film. As microcapsules were prepared by PSS/PAH that used a narrow size distribution SiO_2 particles (300 nm) as templates, so its size were uniformed (a little

larger than 300 nm). While, from image (b), we can obviously find that the microcapsules appear unequally size in (bPEI/PAA)*30-microcapsules composite PEM film. This is because the microcapsules were incorporated in different positions of the film resulting in the depth of embedding differ, and the microcapsules may collapse during the drying process, so the size distribution of the capsules seems be different from that of the silica particles. What's more, the surrounding surface of spherical structures in (bPEI/PAA)*30-microcapsules composite PEM film displays the same smooth surface structures with the (bPEI/PAA)*30 PEM film. This means the surface of the (bPEI/PAA)*30-microcapsules composite PEM film is comprised of bPEI, PAA and microcapsules, rather than only microcapsules. All these phenomena indicate that the microcapsules are integrated into the polymer film by the electrostatic attraction between the positively charged microcapsules and negative charged PEM film, rather than by means of physical mixture. This is because the outmost layer of capsule is PAH, which is positive charged, so, the microcapsule is positive charged. While the PAA is negative charged and lastly assembled, so, PEM film is negative charged. In the process of forming (bPEI/PAA)*30-microcapsules composite PEM film, the positively charged microcapsules are attracted by the negative charged bPEI/PAA-glass substrate, reacting to form composite film. Satish Patil and co-workers also assembled particles on thin film through electrostatic attraction between particles and thin film.[37]

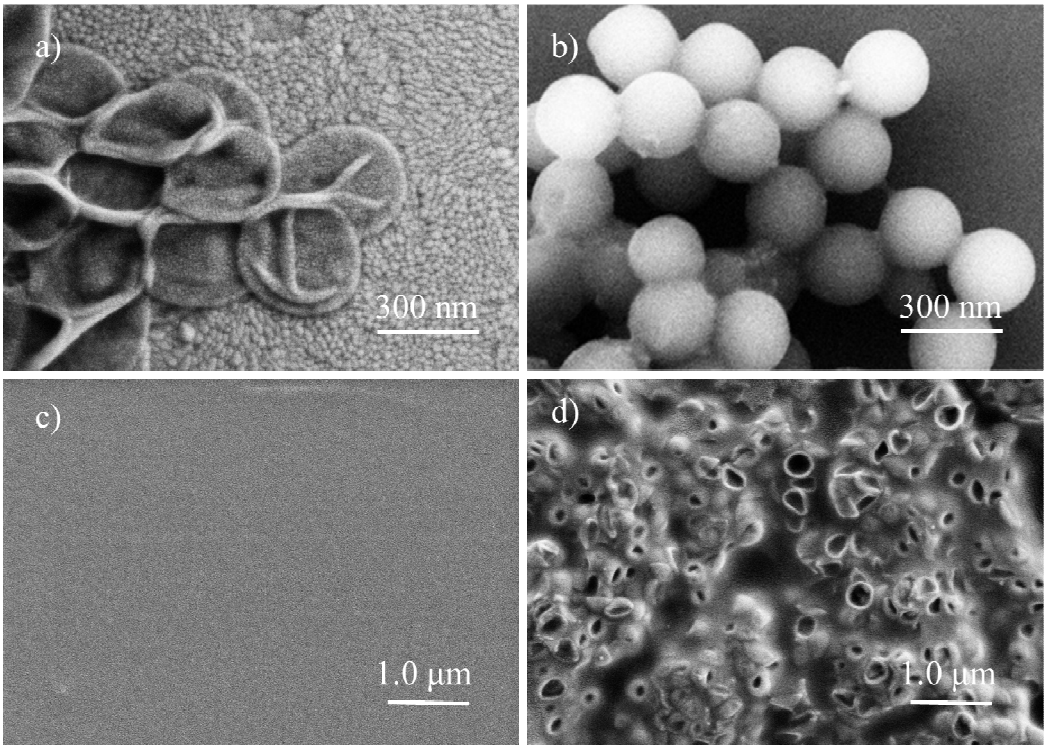

Fig. 3. FESEM images of (a) microcapsules dried at room temperature (b) treated with the freeze-dried technique, (c) (bPEI/PAA)*30 PEM film and (d) (bPEI/PAA)*30-microcapsules composite PEM film dried at room temperature

As the prepared films take place self-healing process under conditions of suitable water or higher humidity, so the wettability of the film surface can be determined as part of the self-healing design.[38] Thus, the wettability of (bPEI/PAA)*30 PEM film and (bPEI/PAA)*30-microcapsules composite PEM film were investigated by measuring their water contact angle, results are shown in Fig. 4. The water contact angle of (bPEI/PAA)*30 PEM film is 53.13°, the water contact angle of (bPEI/PAA)*30-microcapsules composite PEM film is 50.26°, only slightly smaller than (bPEI/PAA)*30 PEM film. When the film is going through the self-healing process, the initiator (water) can diffuse and infiltrate a hydrophilic surface more quickly and easily than the one in a hydrophobic surface, which will result in the

hydrophilic PEM film repairing itself. In theory, all other factors being equal, the smaller the water contact angle of the self-healing PEM films, the more readily the self-healing PEM films will engage in the self-healing process. From the water contact angle results above, conclusion can be drawn that microcapsules have some positive effect on self-healing process of PEM film.

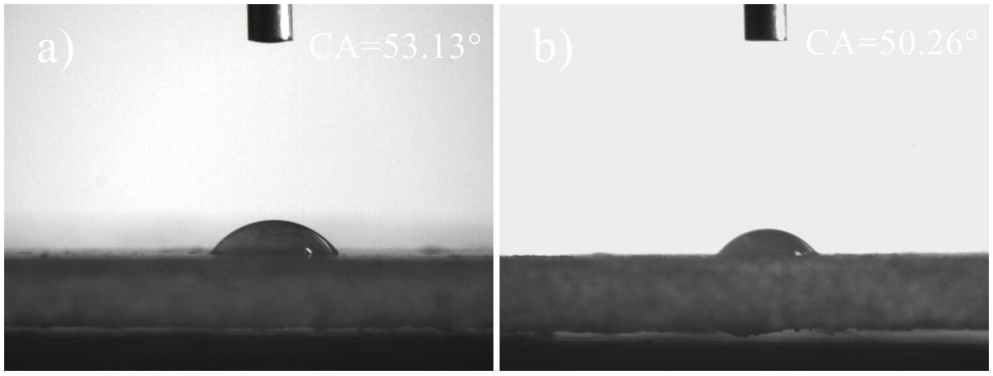

Fig. 4.Water contact angle of (a) (bPEI/PAA)*30 PEM film and (b) (bPEI/PAA)*30-microcapsules composite PEM film

3.2. Self-healing ability and mechanical property of the PEM films

The dynamic self-healing process of the (bPEI/PAA)*30-microcapsules composite PEM film was observed via stereomicroscope. Firstly, the film was divided into a cross with a scalpel, the scratch width was about 20 μm. Fig. 5 (a) is the result of (bPEI/PAA)*30-microcapsules composite PEM film after injury treatment. When a drop of water is injected into the film, the damaged zones of the film can mobile themselves to a certain extent via swelling rapidly, disappear gradually. While, the film without stimulating by water have no change in volume (b). Then, as the water expanding slowly on the film, the damaged zones of the film repair themselves constantly (c). Lastly, when the film is completely infiltrated by water, the scratches can not be found. Meanwhile, when the film meet the water, the original interactions (hydrogen bonds) of the film becomes weak, so the damaged zones can interact with

each other, after removeing the initiator, the hydrogen bonds regenerated, the damaged film completes its self-healing process. Thus the film heals itself completely (d).

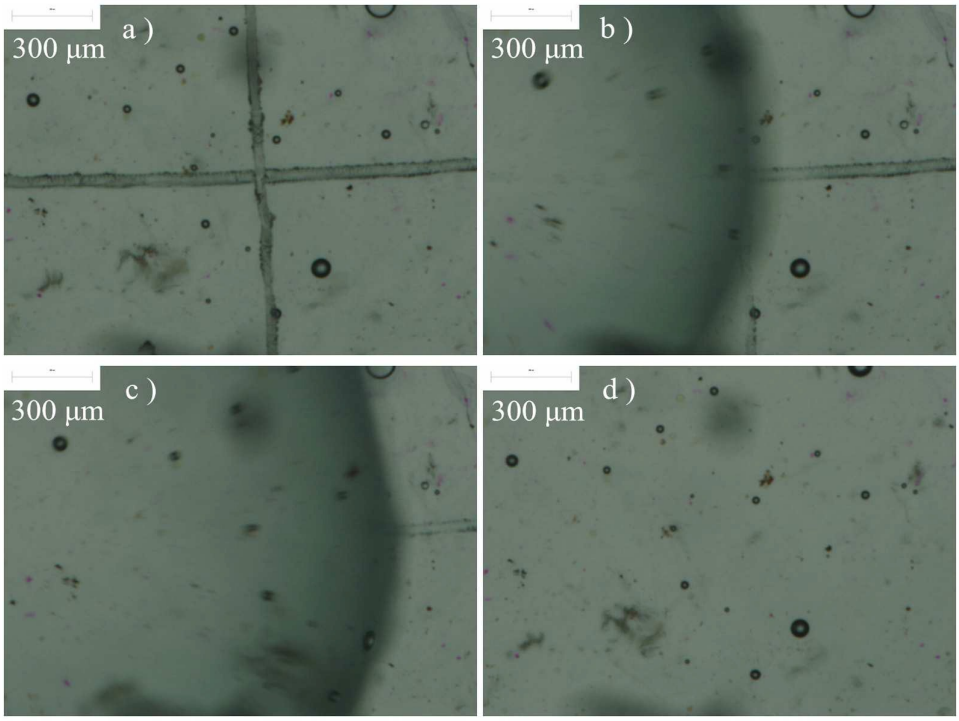

Fig. 5. (a–d) Visual observation of the healing process of (bPEI/PAA)*30-microcapsules composite PEM film, the scale bar is 300 μm.

Nanoindentation was employed to study the different mechanical properties of (bPEI/PAA)*30 PEM film and (bPEI/PAA)*30-microcapsules composite PEM film, mechanical properties of (bPEI/PAA)*30-microcapsules composite PEM film in initial state and self-healed state. The results of the two samples are shown in Fig. 6. From Fig. 6(a), comparing the load-displacement curves of the two samples, one can find that, the load-displacement curves of two samples are almost coincident, indicating the (bPEI/PAA)*30 PEM film and (bPEI/PAA)*30-microcapsules composite PEM film has the same mechanical property. In Fig. 6(b), when the indentation depth in the range of 0-2000 nm, the hardness of

(bPEI/PAA)*30-microcapsules composite PEM film in initial state and self-healed state are the same, when the depth is above 2000 nm, the load-displacement curves of the self-healed (bPEI/PAA)*30-microcapsules composite PEM film become differ from its initial state, but only changes slightly, and its hardness become a little weaker than its initial state. The result indicate that the sample can heal its mechanical property after damaged, which further proved that the (bPEI/PAA)*30-microcapsules composite PEM film has excellent self-healing property.

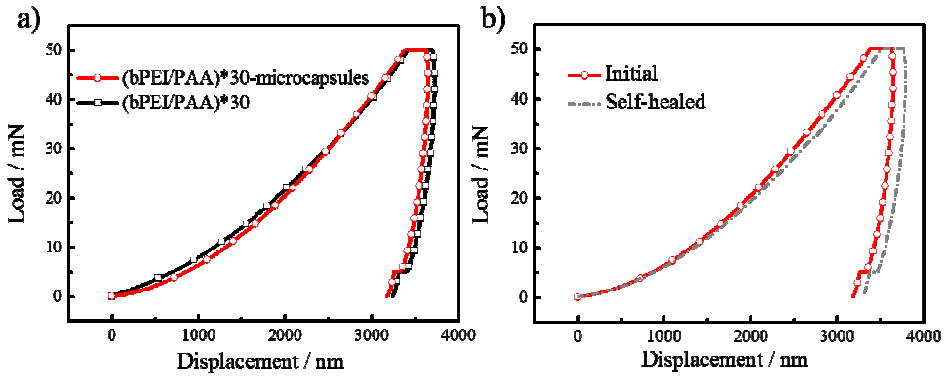

Fig. 6. Mechanical properties of (a) (bPEI/PAA)*30 PEM film and (bPEI/PAA)*30-microcapsules composite PEM film, (b) mechanical properties of (bPEI/PAA)*30-microcapsules composite PEM film in initial state and self-healed state.

3.3. Release and antibacterial ability of the PEM Films

Microcapsules can be multi functionalized by tailoring their composition, structural, physico-chemical and mechanical properties at the nanometer scale. What is more, not only the surface can be modified to alter the functionality but various materials can be sequestered into the microcapsules interior for drug delivery, sensing or catalysis applications.[39] RB is a kind of synthetic dyes with fresh peach that widely

used as model drug molecule. So we use RB as model molecules to evaluate the different release processes between (bPEI/PAA)*30 PEM film and (bPEI/PAA)*30-microcapsules composite PEM film. RB-(bPEI/PAA)*30-microcapsules composite PEM film was obtained by immersing the (bPEI/PAA)*30 PEM film in RB loaded microcapsules solution, (bPEI/PAA)*30 PEM film was also immersed in RB solution to obtain RB-(bPEI/PAA)*30 composite film as control sample. Then immersing the films in water to observe the release process, UV–VIS spectroscopy is used to monitor the content of RB in films, the characteristic absorbance of RB is at 555 nm, which declines with releasing time. The time-dependent releasing process of RB at room temperature are shown in Fig. 7. The RB-(bPEI/PAA)*30 PEM film releases RB relatively rapidly in the initial 120 min and the release rate up to 75%; the sustained releases of RB in water become very slow among 120 to 1120 min; After 1120 min, because there is only a little RB in film and hard to release, so the release rate has almost no change. While the RB-(bPEI/PAA)*30-microcapsules composite PEM film releases RB more evenly, although releases a little quickly in initial 120 min, after that, the release process become slow and steady; Until 1600 min, the release rate changes little. This may because microcapsules have sustained-release function and the incorporated microcapsules endow the films have the same function.

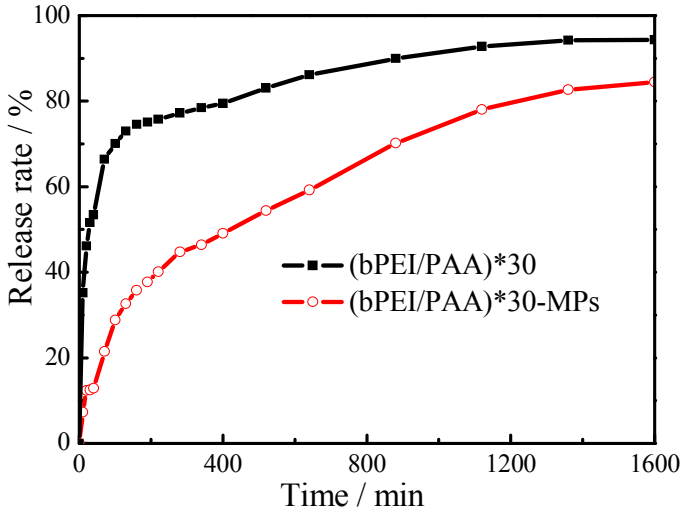

Fig. 7. The release processes of (bPEI/PAA)*30 PEM film and (bPEI/PAA)*30-microcapsules composite PEM film

It is difficult to achieve different functions by grafting hydrophobic molecules directly on the LbL self-healing films, while via "function carriers", microcapsules, this problem can be solved easily. Here, ROX was taken as an example of hydrophobic molecule and was loaded in the prepared microcapsules by immersing the microcapsules in ROX alcohol solution. Then the drug-loaded microcapsules were embedded into the (bPEI/PAA)*30-microcapsules composite PEM film and the antibacterial ability was investigated. Glass substrate coated with ROX-(bPEI/PAA)*30-microcapsules composite PEM film was gently placed on Luria Bertani (LB) agar plate, then *S. loihica* PV-4 was vaccinate though streak plate technique. Glass substrate coated with (bPEI/PAA)*30 PEM film was prepared as control group. After 24 h of incubation, the antibacterial property of (bPEI/PAA)*30 PEM film and ROX-(bPEI/PAA)*30-microcapsules composite PEM film were investigated. The results are shown in Fig. 8. In Fig. 8(b), around the

ROX-(bPEI/PAA)*30-microcapsules composite PEM film, there is a visible bacteriostatic area (the irregular rectangular area with a red line, where present a translucent substrate and there are no yellow *S. loihica* PV-4), while in the control sample, *S. loihica* PV-4 grow around (bPEI/PAA)*30 PEM film tightly (a), indicating that the ROX-(bPEI/PAA)*30-microcapsules composite PEM film can release ROX and retain its activity to restrain the growth of *S. loihica* PV-4, film without be loaded ROX-microcapsules do not exhibit antibacterial ability. The results further proved that the (bPEI/PAA)*30-microcapsules composite PEM film can be easily functionalized with desired properties through assemble functional microcapsules.

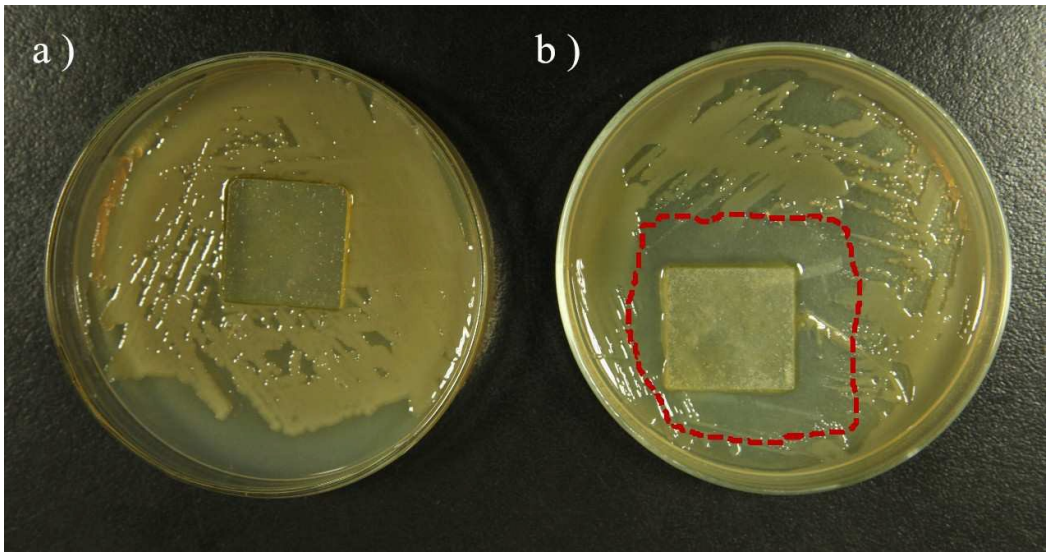

Fig. 8. The antibacterial properties of (a) (bPEI/PAA)*30 PEM film and (b) (bPEI/PAA)*30-microcapsules film

4. Conclusions

We successfully fabricated the self-healing (bPEI/PAA)*30-microcapsules composite PEM film based on LbL self-assembly technique. Then, we try to endow the prepared film desired function through tailoring the microcapsules. In our experiment, the hydrophilic model drug molecule RB and hydrophobic model drug molecule ROX are

all loaded in (bPEI/PAA)*30-microcapsules composite PEM film, release process and antibacterial properties test show that the RB loaded (bPEI/PAA)*30-microcapsules composite PEM film has good sustained-release property, ROX loaded (bPEI/PAA)*30-microcapsules composite PEM film can release ROX and retain its activity to restrain the growth bacterial growth, while (bPEI/PAA)*30 PEM film sustained-release property performances poor and cannot be functionalized with hydrophobic molecules. Given the microcapsules can be readily engineered and functionalized with desired properties, be easily assembled on the PEM film, through this method, different types of desired functional self-healing films can be fabricated and are believed to have practical applications in various devices with enhanced durability and reliability.

Acknowledgments

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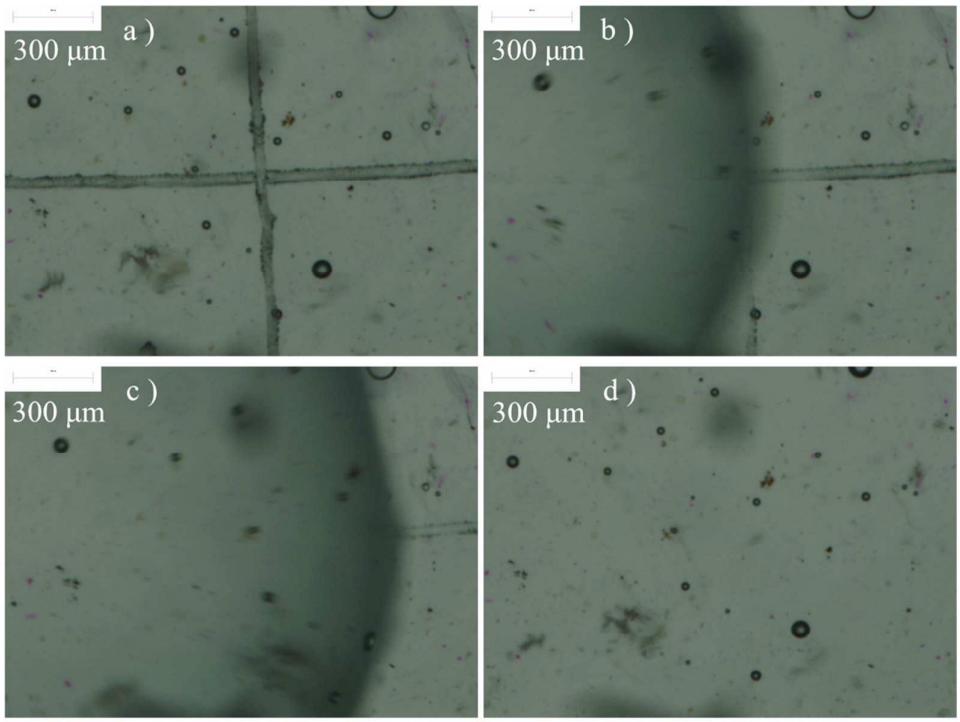

Model molecules can be easily loaded in self-healing (bPEI/PAA)*30-MPs composite film and endow the film with desired functional properties.