Self-healing Cellulose Membranes Prepared by Microcapsules Containing UV-initiated Healing Agents

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Keywords: Self-healing, Photo-initiated, Microcapsules, Cellulose membrane.

Abstract. A photo-initiated microcapsule with a poly(urea-formaldehyde) shell was synthesized through in situ polymerization, in which aliphatic polyurethane acrylate and photoinitiator used as photo-initiated healing agents. Then, the as-prepared microcapsules were mixed into the cellulose solution and coagulated in ethyl alcohol to prepare a self-healing cellulose membrane. The results show that microcapsules successfully encapsulated core materials and owns a thermal stable temperature of 212°C. The self-healing behavior can be observed by confocal laser scanning microscope after the damaged cellulose membrane was irradiated by UV light for 20min. Furthermore, FTIR spectra of self-healed membrane indicated the formation of hydrogen bond between healing agents and self-healing cellulose membrane. This study could provide an effective method for extending the life span of cellulose membrane.

Introduction

Inspired by the survival feature of living organisms, the technology of self-healing has developed rapidly in polymers and polymer composites [1]. Polymer materials always experienced microcracks initially and led to microscopical damage eventually with the influence of environmental or manually factors. However, it is unpractical to precisely locate the damage sites and fixing the cracks in the operation process due to its inherent limits. Therefore, polymer materials processing self-healing capability as an ideal long-term operation has been quickly developed in recent years [2].

Typically, self-healing polymers are classified into two major categories. The extrinsic self-healing system, include polymers embedded with microcapsules, hollow fibers, etc. Intrinsic self-healing polymers, i.e. polymers with dynamic covalent bonds or polymers can be repaired by thermodynamics [3]. Notably, microcapsule-type self-healing systems have been extensive investigated due to its ease of preparation and applicability [4]. Traditionally, the self-healing technology based on microcapsules has been mostly applied in protective coatings or embedded in the cement matrix to protect the material from deterioration [5, 6]. A number of studies investigated other application on other matrix i.e. poly(ether sulfone) membrane[7], glass fiber reinforced epoxy composites[8]. However, among them, there are some drawbacks including catalyst availability, environmental toxicity, stability, healing time and material processing. In addition, challenges existed in developing self-healing systems based on different healing matrix.

Herein, we prepared a self-healing regenerated cellulose membrane, giving an application of self-healing technology based on microcapsules. To improve the healing efficiency of cellulose membrane, an all-in-one photo-initiated microcapsules with a poly(urea-formaldehyde) (PUF) shell was fabricated through in situ polymerization and embedded into the cellulose membrane. Photo-initiated self-healing system by UV light is an environmental-friendly, cost-effective and practical strategy[9]. Moreover, prior investigations has noted that polyurethane acrylate has good adhesion with regenerated cellulose membrane and can be cured rapidly under UV irradiation[10, 11], so aliphatic polyurethane acrylate and photoinitiator was chosen as the healing agents in our
study. As shown in Scheme 1, the core material will released into the damaged area, and the membrane will be healed by exposure to UV light.

Scheme 1. Preparation of microcapsule based self-healing cellulose membranes.

Experimental

Material and methods: Pulp cellulose (degree of polymerization, 500) with α-cellulose content of 93.8% provided by Shandong Hailong Co. Ltd., China. Urea, ammonium chloride, resorcinol, aqueous formaldehyde solution (37wt%), sodium dodecylbenzenesulfonate (SDBS), 1-octanol, trithanolamine (TEA), sodium hydroxide were purchased from the Chinese Medicine Group. Aliphatic polyurethane acrylate RJ423 (degree of functionality, 6) and 1,6-hexamethyl-diol diacrylate (HDDA) were purchased from Guangzhou Lihou trading Co. Ltd., China. 2-hydroxy-2-methyl-1-phenylpropan-1-one (photoinitiator 1173) and rhodamine B were purchased from TCI. All chemicals were analytic grade reagents or above and used without further purification.

The self-healing microcapsules with a poly(urea-formaldehyde) shell were fabricated via in situ polymerization refer to the reported investigation [12], using aliphatic polyurethane acrylate RJ423, HDDA and photoinitiator 1173 as core material (4.9:4.9:0.2 by weight), with a shell-core ration of 1:1. Pulp cellulose was dried at 80°C to a constant weight. Then 7.5% of NaOH, 11% of urea, 81.5% of deionized water was added to a 250ml beaker as a solvent of cellulose according to the previous research[13]. After the solvent was precooled to -12°C, 3%wt of cellulose was added to the solvent immediately and kept stirring vigorously for 5 min to obtain a transparent cellulose solution. The solution was centrifugation at 8,000r/min for 10 min to remove the air bubbles and slightly remaining undissolved part. Then, a certain mass fractions of microcapsules were dispersed into cellulose solution. The solution was cast on a glass plate with a thickness of 2mm, and then coagulated with absolute ethyl alcohol at ambient temperature to obtain a self-healing cellulose membrane. For confocal laser scanning microscope (CLSM) images, the coagulation bath was added with 0.03wt% of rhodamine B. After the membrane was obtained, it was rinsed with pure ethanol and dried at ambient temperatures and indoor conditions for 48h to avoid the core material been solidified. Then sample cellulose membrane was damaged with a slice blade manually to simulate the microcracks in the membrane. Finally, the membrane was under UV irradiation for 20 min at room temperature to cure the outflowed healing agents.

Characterization: Optical microscopy (OM, NIKON ECLIPSE E-400 POL) was used to monitor the reaction of microcapsule preparation and observe the healing process. Scanning electron microscope (SEM, TM-1000, Hitachi) was used to assess the surface morphology of the microcapsules and self-healable cellulose membranes. FT-IR spectroscopy was used to characterize the cellulose membrane with Fourier transforms infrared analysis (Nicolet 6700, Thermo Fisher, USA). Self-healing behavior of microcapsule based cellulose membrane was observed by confocal laser scanning microscope (Leica SP5). The images were obtained using a 10×objective lens and a 4×software zoom at an excitation wavelength of 514nm. 3D images were constructed by Imaris 6.2 software (Bitplane Co., Switzerland). Fractured surface SEM micrographs and energy dispersive spectroscopy (EDS) analysis were conducted by a Quanta 400 FEG field emission scanning electron microscope (Hitachi S-4800). Thermogravimetric (TG) analysis was carried out on 204 F1
analyzer (Netzsch, Germany) at the heat rate of 10 °C/min and the temperature was ranged from 50 to 900°C.

Results and Discussion

Figure1 shows the different stages of self-healing microcapsules were monitored in the reaction using optical microscope. At the first stage (Figure1(a)); the core material was emulsified into the solution of 0.5wt%SDBS aqueous solution to form a uniform oil in water system through electrostatic repulsion. Then, the pH of the emulsion was adjusted to 2~3, with temperature raised, the poly (urea-formaldehyde) shell began to form (Figure1(b)). After the reaction was kept for 3~4h, microcapsules was formed and deposited in the bottom of flask. The morphology of microcapsules was also observed by optical microscope. Figure1(d) shows the microcapsule is uniform spherical. The surface morphology of self-healing microcapsules was investigated by scanning electron microscopy (SEM). As shown in Figure1(e) and Figure1(f), the prepared microcapsules have a rough external surface and a smooth internal surface with a wall thickness of 1.29–2.95μm. The mean diameter of microcapsules is 102μm. The deposit sediment on the microcapsules is the redundant shell material.

![Figure 1. OM images of the (a) core emulsion (b) shell-formation process (c) suspension after reaction finished (d) dried microcapsules (scale bar is 100μm) and SEM images of (e) integrated microcapsule (f) broken microcapsule.](image)

Figure 2 shows the SEM fractured surface micrograph of self-healing cellulose membrane and energy dispersive spectroscopy (EDS). As seen from Figure2(a), the microcapsule was ruptured and shows good interfacial adhesion with cellulose membrane. As seen from Figure2(b), Figure2(e), Figure2(d), the scattered dots in the elemental mapping indicated the distribution of O,C,N elements in the fracture surface [14].The concentration of the indicator element (nitrogen) in the region of microcapsules implied the successfully encapsulation of core materials.

![Figure 2. SEM fractured surface micrograph of (a) self-healing cellulose membrane and EDS analysis of fractured surface with (b) oxygen (c) carbon (d) nitrogen as indicator element.](image)

The thermal stability of PUF shell and self-healing microcapsules were characterized by TGA analyses. The curve was obtained under nitrogen atmosphere at heating rate of 10°C/min. As shown in Figure3(b), the initial weight loss of about 10% between 0°C and 110°C due to the remove of the
adsorbed formaldehyde and water in the surface of microcapsules. The microcapsules began to decompose rapidly at 110°C due to the decompose of core material in the microcapsules which exists cracks. When the temperature up to 212°C, both of the PUF shell and microcapsules has a subsequent decomposition, indicating that the microcapsule lost the protection of the shell. The weight loss over 305°C was the further degradation of remainder shell and core material. To conclude, the thermal stable temperature of microcapsules was 212°C.

![Figure 3. TGA curves of (a) PUF shell and (b) self-healing microcapsules.](image)

The self-healing behavior of microcapsule in cellulose membrane was examined by confocal laser scanning microscope. As shown in Figure 4, the prepared self-healing cellulose membrane has a thickness of about 104–138um. The sectional confocal images of damaged cellulose membrane (Figure 4(e)) and healed cellulose membrane (Figure 4(f)) demonstrated that the crack was filled with the healing agents, the membrane was successfully healed.

![Figure 4. Confocal laser scanning microscope images of (a) pristine cellulose membrane (b) damaged cellulose membrane (c) self-healed cellulose membrane and sectional images of (d) pristine cellulose membrane (e) damaged cellulose membrane (f) self-healed cellulose membrane. (scale bar is 50um).](image)

The ATR-FTIR spectra of cellulose membrane in Figure 5(a) shows a characteristic absorption peak of cellulose structures at 3336cm⁻¹,1158cm⁻¹ attributed to the -OH stretching vibration, C-O-C asymmetric stretching vibration, respectively. Stretching vibration of C-H in –CH₃ and –CH₂ centered at 2906cm⁻¹. While as is shown in Figure 5(b), -OH stretching vibration in self-healing cellulose membrane located in 3320cm⁻¹ which has shifted to lower wavenumbers and a broader peak compared to the spectrum of pristine cellulose membrane, suggesting the enhancement of hydrogen bonding, implying the formation of hydrogen bond between C=O in the polyurethane acrylate structure and –OH groups in the cellulose structure. Besides, Figure 5(b) shows the absorption peak at 1730cm⁻¹ attributed to the core material, indicating the outflowing of core material in self-healing cellulose membrane.
Conclusions
This paper introduces the synthesis of microcapsules containing UV-initiated healing agents and its self-healing behavior when embedded in cellulose membrane. The results have demonstrated that the microcapsule successfully encapsulated the photo-irradiated healing agent which is confirmed by SEM and EDS analysis. The thermal stable temperature of microcapsules is 212℃ according to the TG analysis. From the confocal laser scanning microscope images, it showed the damaged cellulose membrane was successfully healed after irradiated under UV light for 20min. FTIR spectra demonstrated there were hydrogen bonds forming between the healing agents and cellulose. In sum, it will be a potential method to extend the life span of cellulose membrane.

Acknowledgements
The research was supported by National Natural Science Foundation of China (no.51403032) and Key Laboratory of High Performance Fibers & Products, Ministry of Education, Donghua University.

References


