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Preparation of thermochromic liquid crystal microcapsules for intelligent functional fiber

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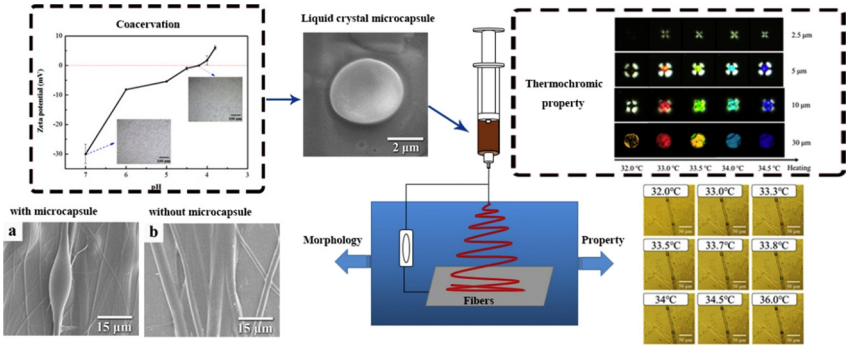
HIGHLIGHTS

- Cholesteric liquid crystals microcapsules were prepared via complex coacervation method.
- The optimal particle size of cholesteric liquid crystals microcapsules with good thermochromic property is 5–30 μm.
- The intelligent functional fibers shows color change from red to blue as the temperature increases.

GRAPHICAL ABSTRACT



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ABSTRACT

Cholesteric liquid crystals microcapsules (CLCM) were prepared via complex coacervation method, which were further used as thermochromic materials in an intelligent functional fiber. The morphology of CLCM with core-shell structure was confirmed by SEM and TEM images. According to the TG results, CLC core took 52 wt% of the microcapsules. Thermochromic property of the CLCM was closely related to its particle size, and CLCM in the range of 3–30 μm had excellent thermochromic property producing color progressively moving from red to blue as the temperature was raised. The CLCM were added to polyvinyl pyrrolidone (PVP) solution and CLCM/PVP fibers were prepared by electrospinning method. The thermochromic performance of CLCM/PVP fibers was in accordance with CLCM, and the optimal particle size of CLCM for preparing CLCM/PVP fibers was 3–10 μm.

1. Introduction

Intelligent functional fibers exhibit physical or chemical changes in response to external stimuli such as temperature [1,2], pH [3], chemicals [4], electric fields [5] and magnetic fields [6], which provides many possibilities in the application of drug delivery systems, self-repairing materials, smart sensors and intelligent textiles [7–10]. Thermochromic fibers as a kind of intelligent functional fibers, undergoing colorimetric transitions upon application of temperature, have attracted much attention in temperature indicators, wearable display, design accessories and baby protective equipment [11–14].

An effective way to endow fiber with thermochromic behavior is to embed thermochromic materials in the fiber [15,16]. These thermochromic materials are mostly found in conjugated organic molecules such as dyes [17], conjugated polymers [18] and cholesteric liquid crystals [19,20]. Cholesteric liquid crystals (CLC) arouses wide concern

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because of its variety of color changes, high sensitivity and quick response. CLC can offer a wide variety of color changes due to the characteristic helical structure reflecting circularly polarized component of light. The wavelength of the reflecting circularly polarized light depends on the pitch ***p*** of the CLC, which is defined as the distance of liquid crystal molecules rotate 360° along its helical axes [21]. The pitch length is extremely sensitive to temperature so that the reflected light changes with the variation of temperature.

Electrospinning has been widely adopted to incorporate functional additives into electrospun fibers [22–26], which also applies to CLC/polymer electrospun fibers. J. Lagerwall et al. [27] utilized coaxial electrospinning with separately liquid crystal and polymer fluids to produce core-shell structure fibers. West et al. [28] reported forming liquid crystal/polymer fibers by electrospinning a homogeneous solution of liquid crystals and polymer. However, thermochromic property of the CLC is closely related to number of ***p***, which is affected by the distributions of CLC in the fibers. When CLC are directly added in electrospinning solution to fabricate CLC/polymer fibers, CLC are not uniformly distributed throughout the fiber, which seriously deteriorates thermochromic performance of CLC/polymer fibers. Moreover, CLC cannot easily fix on the fibers with the risk of leaking out of fibers due to the liquidity of CLC, affecting their thermochromic property.

Therefore, CLC microcapsules (CLCM) are designed before electrospinning process, in order to control the content of CLC and protect CLC against leakage for optimizing their thermochromic performance. The effects of CLCM particle size on the thermochromic property were evaluated. Then these CLCM were added to PVP solution and CLCM/PVP fibers were prepared by electrospinning method. It is expected that the CLCM/PVP fibers have potential in preparing intelligent functional fibers, for instance, applying in visual temperature indicator.

2. Experimental

2.1. Materials

Cholesteryl nonanoate (CPE, purity >95%) was obtained from Alfa Aesar Co., Ltd., USA. Cholesterol oleyl carbonate (COC, purity >95%) were supplied by Tokyo chemical industry Co., Ltd, Japan. Gelatin and acacia were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. Acetic acid (HAc) and sodium hydroxide (NaOH) were analytical grade and supplied by Sinopharm Chemical Reagent Co., Ltd., China. Polyvinyl pyrrolidone (PVP, Mn = 1,300,000) was analytical grade and supplied by Boai NKY Pharmaceuticals Ltd, China. All chemicals were used as received.

2.2. Preparation of thermochromic liquid crystal microcapsules

The liquid crystal mixture consisting of equal weight of COC and CPE was homogenized at 60 °C and then added to an acacia solution (2.5% acacia in water, w/w) to disperse by a high-speed emulsification (IKA, Germany) to make CLC emulsion. After the addition of a gelatin solution (2.5% acacia in water, w/w), the pH value of the emulsion was adjusted to 4 by drop-wise addition of acetic acid solution to induce coacervation. Subsequently, the coacervated emulsion was cooled down to 0 °C, and methanal solution (37% methanal in water, w/w) was added and the pH value was adjusted to 8.5 so as to promote crosslinking of gelatin and acacia. During the process, the agitation cannot be stopped to prevent aggregation.

2.3. Electrospinning process

The electrospinning apparatus included a high-voltage supply (Dongwen Co., Tianjing, China), a microinfusion pump (Medical Instrument Co., Zhejiang, China), a 20 ml syringe with a metal needle and aluminum foil as the collector. Each solution was drawn horizontally from the needle tip by the electrostatic force generated from the high voltage applied between the tip and the collector. It formed a Taylor cone and jetted through the needle tip to the collector. The distance between the needle tip and the collector was kept at 15.0 cm. The applied voltage was set at 20 kV. The fibers deposited on the aluminum foil collector in the form of a nonwoven mat after the evaporation of the solvent. The fibers were dried under vacuum before they were detached from the aluminum foil.

2.4. Measurement

2.4.1. Zeta potential

The samples were injected into the measurement cell. The electrical charge measurements of the solutions were performed at 25 °C using a Zetasizer Nano ZS 90 (Malvern, UK), with reproducibility being checked by performing three repeated measurements.

2.4.2. Optical and polarized optical microscopy (OM/POM)

Optical and polarized optical microscopy images were collected using polarized light with sample between crossed polarizers by an inverted microscope (Sunny Optical Technology Co., Ltd, China). The images were taken with a color CCD camera (LUXOPTO Co., Ltd, China) under polychromatic illumination produced by a halogen lamp. All observations were carried out at an ambient temperature of 25 °C.

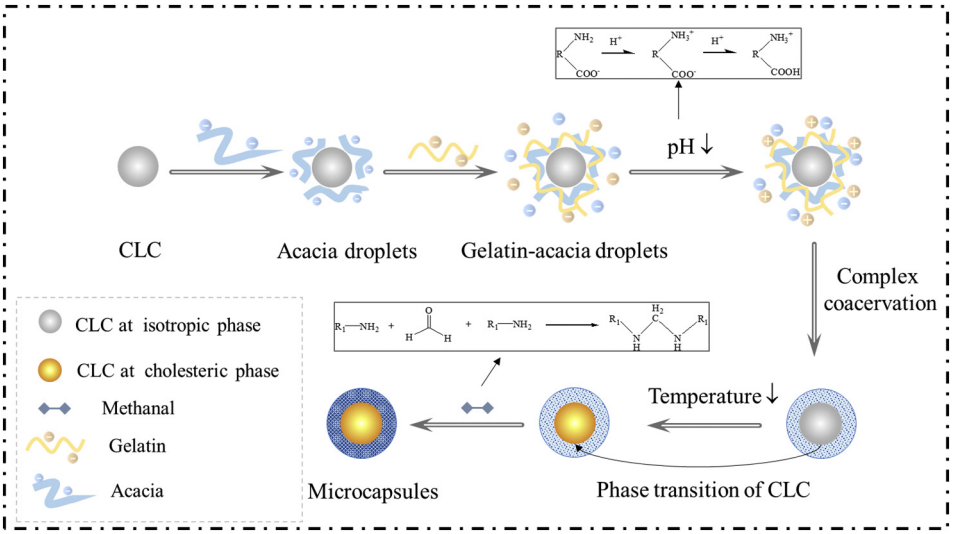

Fig. 1. Fabrication of CLCM by complex coacervation.