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Letter

Visual and flexible temperature sensor based on a pectin-xanthan gum blend film

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ABSTRACT

With the rapid progress in electronics technology, there has been an increasing trend towards making electronic devices light, flexible, and wearable. This study investigates an artificial skin-like temperature sensor based on pectin and xanthan gum. The highly flexible and transparent temperature sensor that was fabricated was simple in structure and the sensitivity was 53–130%°C^{-1} in the temperature range of 26 °C–50 °C. The temperature-sensitive thermochromic ink that was added to the sensing film enables the visualization of the temperature-sensing process. This smart thermal sensor can be widely applied in industries as electronic skin, human body temperature measurements, and environmental monitoring, etc.

1. Introduction

In recent years, with the rapid progress in electronics technology, there has been an increasing trend towards making electronic devices light, flexible, and wearable [1,2]. Flexible electronic skin [3–5] has been developed for prostheses that can help reproduce the natural sensibility of human skin. The electronic skin, as an ideal model system, has numerous sensory receptors that allow the perception of external stimuli like temperature changes [6,7]. The concept of electronic skin was firstly proposed by Rogers, who developed an initial prototype composed of multifunctional diodes, wireless power coils, radio-frequency generators, and other components [8]. This epidermal device he made was very sensitive to changes in temperature and thermal conductivity. Subsequently, He fabricated a stretchable active temperature-sensing matrix based on polyaniline (PANI) nanofibers that contained thin-film transistors made from single-walled carbon nanotubes [9–13]. Although these systems showed performances that reached or exceeded the temperature-sensing capabilities of human skin, composites based on a conductive polymer(like PANI)matrix operate in a too narrow temperature range and have uncertainty on the current value corresponding to the same temperature [14]. Therefore, there is a need to develop flexible artificial skins with a higher temperature sensitivity, responsiveness and stable operational range.

Researchers have been able to develop electronic skins that are highly sensitive and can identify a temperature change of 1% [5], where the electronic skin was made from pectin derived from plant cell walls. Pectin is made of very structurally and functionally complex, acid-rich polysaccharides [16] and is an essential structural component of cell walls that binds ions and enzymes [17]. Pectin membranes hold significant promises with respect to the realization of temperature-sensing artificial skin, owing to their inherent flexibility, chemical stability, as well as simple and low-cost fabrication processes [15]. However, the characteristics of the high brittleness and the high water absorptivity limit their use in artificial skin [20–22].

Here, we report a visual and flexible temperature sensor made of pectin, xanthan gum, and temperature sensitive ink. This is a new type of temperature sensor with high sensitivity. The addition of xanthan gum improves the mechanical properties of the films, such as flexibility and elongation at break, while the temperature-sensitive ink allows the visualization of temperature changes. The color change of the sensor with variations in temperature is reversible that increases the safety factor of thermometer-related systems.

2. Experimental section

We used commercially available citrus-based low-methoxylated pectin (Food grade, Anhui Zhongnan Biotechnology Co., Ltd.). The degree of methylation of the pectin sample was 30%, while its galacturonic acid content was 65%. The pectin powder (2.5%, w/v) and xanthan gum powder (CAS:11138-66-2; 0%, 0.4%, 0.5%, 0.6% w/v) were dissolved at 80 °C in deionized water and stirred at 800 rpm until a uniform solution was obtained. To have the films prepared using this solution, we prepared a 32 mM $CaCl_2$ (Alfa Aesar, calcium chloride, anhydrous, porous, 93%) solution (corresponding to a [Ca^{2+}]/

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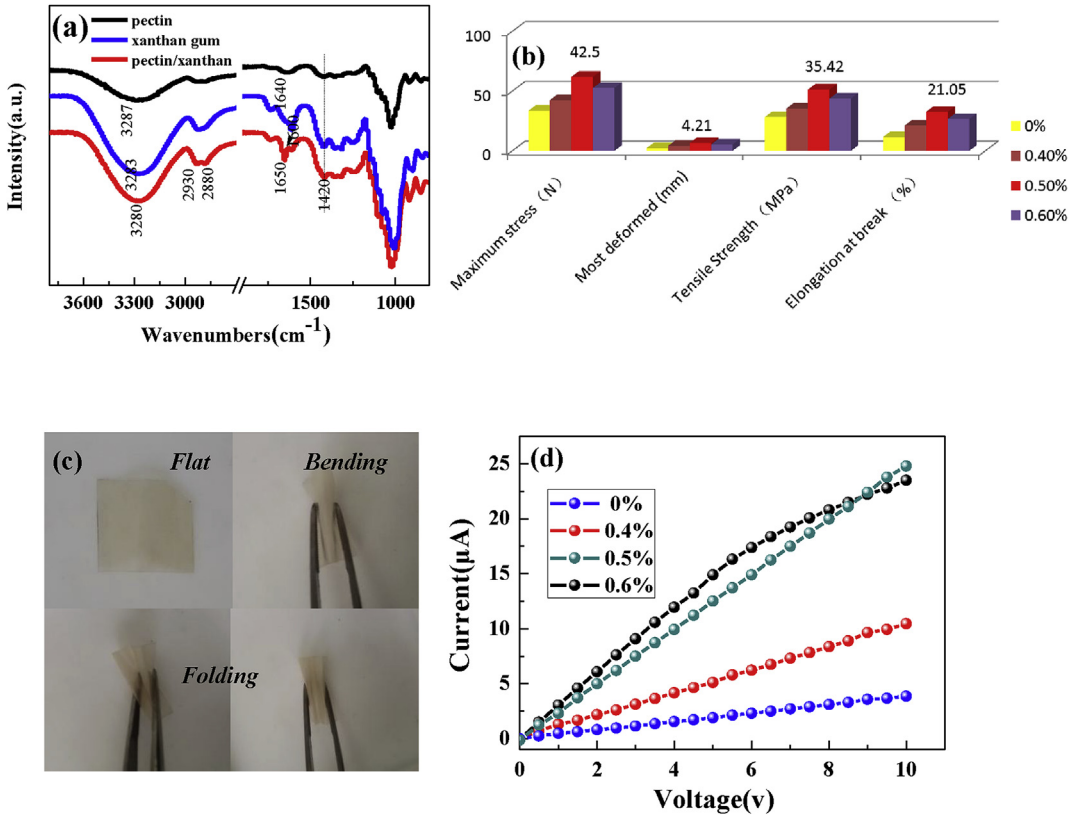

Fig. 1. a) FT-IR spectrogram of pectin, xanthan gum and blend film. b) The mechanical properties (including tensile strength, elongation at break, etc.) of the xanthan gum blend films at different concentrations (0%, 0.4%, 0.5% and 0.6% w/v). c) The physical behaviors of the blend film in different states. d) The typical current-voltage characteristics of the xanthan gum blend films at different concentrations.

$2[COO^-] = 1$). This $CaCl_2$ solution and glycerol (Analytical pure, 0.5 ml) were added in a dropwise manner to the solution by titration, and the solution was stirred at 1200 rpm to form a homogeneous sol. This sol was poured into an 8 × 8 cm polytetrafluoroethylene template and dehydrated in a drying oven at 60 °C. The resulted blend films with different concentrations of the xanthan gum were subsequently removed from the mold.

To fabricate visual and flexible pectin/xanthan gum-based temperature sensors, 80 nm thick Cu was thermally evaporated through a mask at a pressure below 10^{-5} mbar. The electrode-bearing film was placed on a polyimide film substrate. The electrical contacts were made of carbon tape or copper foil, and an insulating polyimide film was deposited on top. To produce the skins, we could also deposit the pectin solution directly on different substrates (for example cellophane, polydimethylsiloxane (PDMS), or SiO_2). The color-changing inks we used were manufactured by Dongguan Yanye Chemical Technology Co., Ltd. The ink is an aqueous temperature-change material having a particle size of about 1–10 μm. The temperature range in which the ink can change color is 34–37 °C. Above 37 °C, the ink becomes colorless.

Fourier transform infrared spectroscopy (FTIR) analysis was performed using a Varian 2000 Scimitar spectrometer in the range of 500–3700 cm^{-1}. A 10 k (maximum sustained tension) universal testing machine was used to characterize the mechanical properties of the sensor. For evaluations of the temperature sensor, it was fixed to different heat sources (20–60 °C) and the electrical performance was measured using a Keithley 2400 system at 5–10 V.

3. Results and discussion

3.1. Structure analysis and electrical properties of the blend films

We fabricated films by casting a pectin solution in a mold (see Experimental Section); the pectin-xanthan gum was cross-linked in a $CaCl_2$ solution and dehydrated in vacuum to obtain a transparent film. The possible interactions between the pectin film and the xanthan film were further clarified by analyzing the FT-IR spectra of the pectin/xanthan blend film (0.4%) (Fig. 1a). The strong absorption bands at 3287 and 3283 cm^{-1} are attributed to the symmetrical stretching vibration of O-H stretching peak of pectin and xanthan film, while the peak of pectin/xanthan blend film shifted to a lower wavenumber at 3280 cm^{-1}, implying the formation of hydrogen bonds between the pectin and the xanthan. In the FT-IR spectrums of the three films, the bonds of 2930, 2880, 1740, 1420 and 1010 cm^{-1} were assigned to the asymmetric and symmetric vibration of the C-H stretching vibration, the C=O stretching vibration of the carboxylic acid group, the O-H deformation of the carboxylic acid group, and the symmetric C-O stretching vibration, respectively. The characteristic vibrational bands of the three films presented at 1640, 1600 and 1650 cm^{-1}, respectively, revealed the formation of the intermolecular hydrogen bonds between carboxylic groups with hydroxy groups or carboxylic groups in the film. This kind of non-covalent interactions endowed the film with the desirable mechanical properties.

In view of the FT- IR analysis, we studied the mechanical properties of the blend films with different concentrations of xanthan gum (Fig. 1b). The film thickness is about 120 μm and size is 8 cm × 8 cm. All samples were tested at 30 °C. With the increasing concentrations of xanthan gum, all of the maximum stress, maximum deformation, tensile strength and elongation at break of the blend films showed a trend of first increase and then decrease. When the concentration of xanthan gum reaches about 0.5%, a maximum appeared. Fig. 1c is the digital camera image showing that the blending films (0.5%) can be bended and folded. Fig. 1d shows typical current-voltage (*I–V*) characteristics of the blend films with different xanthan gum concentrations. Compared with the pure pectin film, the *I-V* curve of the pectin film doped with