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Morphology and properties of thermal/cooling-gel bi-phasic systems based on hydroxypropyl methylcellulose and hydroxypropyl starch

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ABSTRACT

The miscibility between two gels with largely different gelation behaviors is an interesting topic both scientifically and practically. This paper reports a novel bi-phasic system based on two natural polymers, hydroxypropyl methylcellulose (HPMC) which has a thermal gelation behavior, and hydroxypropyl starch (HPS) which has a cooling gelation property. While both biopolymers have the same glucose unit grafted with propylene oxide, and are compatible to a certain degree, they were observed immiscible because of their different gelation behaviors. The immiscibility of these two compatible polymers could result in special structures leading to different blend film properties. Regarding this, the morphology, thermal transition, mechanical properties and oxygen barrier property could be well tailored by the ratio of two biopolymers and the environmental conditions. The knowledge obtained from this work could be useful for understanding other similar systems with desirable structure and properties.

1. Introduction

To cope with the property limitations of individual polymers, achieve specific or new material properties, reduce product prices, and to expand the applications in different sectors, blending two or more polymers is one of the most effective and applicable methods widely practiced [1–5]. However, most polymer blends are immiscible or incompatible on a molecular scale for thermodynamic reasons [6,7]. On a larger scale, the degree of miscibility of polymer blends may also vary to a great extent, due to phase separation, incompatibility, and/or various levels of mixing [6,8]. Moreover, the miscibility of polymer blends is of such underlying importance to determine the morphology and final properties. Regarding this, for example, mechanical properties can be optimized by controlling the blend morphology [1,9]. Consequently, it is highly significant to understand the miscibility and morphology of blend systems.

Hydrogel, which is defined as a three-dimensional network system of polymer chains and water that fills the space between the macromolecules, constitute a group of polymeric materials that have been widely used [10–15]. Many hydrogels are reversible, as molecular entanglements and/or secondary forces such as ionic, H-bonding or hydrophobic forces play the main role in forming the network [16,17]. Hydrogels can undergo gelation at a certain environmental condition and may dissolve again by changing the external factors back to their original states [11]. They are different from traditional thermosetting materials which are a network of covalent bonds joining different macromolecular chains by cross-linking (e.g., rubber and polyurethane), of which the cure process is irreversible. Generally, there are two main groups of multi-phasic polymer blends: blends containing only none-gellable polymers (which cannot undergo gelation individually), and blends containing at least a non-gellable polymer and a gellable polymer, both of which were widely studied. For the former group, congelation can be commonly achieved when the polymers are mixed and interacted with each other, which may be accompanied by additional physical treatment (thermal, UV, etc.) [18,19]; and the latter group of materials undergo congelation based on the solidification

Abbreviations: HPMC, hydroxypropyl methylcellulose; HPS, hydroxypropyl starch.

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of the gellable polymer [20,21]. However, blends based on multiple gellable polymers with largely different gelation behaviors have been seldom studied.

Natural polymers from renewable resources have attracted great attention over the last decades due to a series of reasons including environmental concerns, limitation in petroleum resources, and demands for greater safety and better health for humans. A great majority of natural polymers are hydrogels. For example, hydroxypropyl methylcellulose (HPMC), also called hypromellose, is a non-ionic derivative of cellulose, and has abundant availability, good processibility, and prominent film-forming properties [22–24]. It is one of the most widely used cellulose derivatives for producing edible and biodegradable films [24–26]. HPMC films are strong, flexible, fully transparent, odorless, tasteless, oleophobic. However, HPMC films have insufficient barrier properties [25,27–31]. Besides, its high prices limit its general applications even for pharmaceutical products as medicinal capsules [32–36]. Therefore, it is imperative to improve the processibility and performance, as well as to decrease the costs, of HPMC. Hydroxypropyl starch (HPS) is one of the most promising materials to reduce the costs of HPMC films, as it is a popular low-price food ingredient [31,37] and has good film-forming property [38–43].

Chemically, both HPS and HPMC are polysaccharides consisting of the same chemical unit, glucose, and also both are modified by propylene oxide. Thus, HPMC should have good compatibility with HPS. However, HPMC has a reversible thermal gelation property (which dissolves in water at a low temperature and congeals at a high temperature) and HPS has a reversible cooling gelation behavior (which undergoes gelation during cooling and then upon heating again solates). This makes it difficult to achieve a blend of two polymers with high miscibility and phase distribution. Nevertheless, theoretically, HPMC and HPS can influence the gel properties of each other for obtaining a certain balance. Therefore, the miscibility and phase transition of the HPMC/HPS blends are important and interesting scientific issues which can be applied to other similar bi-phasic systems.

The aim of this work was to use HPMC/HPS as a model for understanding the morphology and properties of thermal/cooling-gel bi-phasic systems. The ratio of the two components in the films, which have different inherent natures, could greatly influence the morphology and properties of the blends. Thus, the main focus in this work is on the effect of HPS/HPMC ratio which could affect the microstructures and inter-phases of HPMC/HPS blend films, studied by scanning electron microscopy (SEM), optical microscopy, and dynamic mechanical analysis (DMA). Oxygen permeability, thermostability, mechanical and optical transparency properties were also evaluated, as they are important properties to be used as food packaging films and coatings. The microstructural analysis of the films in the current study would give significant information about the arrangement of the components in the system, which is relevant to understanding the water barrier, mechanical or optical properties [44]. Regarding this, films prepared from high concentration biopolymer solutions were in particular studied as it is more relevant to manufacturing situations.

2. Materials and methods

2.1. Materials and film preparation

A commercially-available pharmaceutical-grade HPMC (HT-E15, from Hopetop Pharmaceutical Company, China: viscosity (2%): 6.3 mPa; pH 6.0; methoxyl content on dry basis: 29%; hydroxypropyl oxygen content on dry basis: 8.4%) was used in this work. This is a reversible thermal gel, which congeals ($G' > G''$) at 49 °C upon heating and then during cooling solates ($G'' > G'$) at 32 °C, determined from rheological measurement (TA Discovery HR-2). A food-grade hydroxypropylated cornstarch (HPS) (A1081) with a molar substitution (MS) of 0.11 was supplied by Penford (Australia). The starch paste (gelatinized starch in water) has a reversible cooling gelation property. It congeals ($G' > G''$) at 51 °C during cooling and solates ($G'' > G'$) at 70 °C while heating, detected from rheological tests (TA Discovery HR-2). Poly(ethylene glycol) (PEG 400) with a molecular weight (MW) of 400 was purchased from Sigma-Aldrich.

Solutions obtained by dissolving HPS and HPMC (15% totally) and adding PEG as the plasticizer (3%) in water were used for film forming. Five films containing different HPS/HPMC ratios (10:0, 7:3, 5:5, 3:7, and 0:10, w/w) were prepared in this work. Specially, HPS and HPMC (in powdery form) were mixed firstly then dispersed in 70 °C water for 30 min with continuous stirring, which was maintained at 95 °C for 1 h to allow full gelatinization of HPS. After that, the HPS solution were slowly stirred while the temperature was quickly reduced to 70 °C and kept at this temperature for 40 min before film casting (while all the samples maintained good liquidity). To obtain films with constant thickness, 20 g of each solution was dispensed on a Petri dish (15 cm diameter) and then kept at 37 °C for about 7 h. The films were then removed from the dishes and kept under different relative humility (RH) conditions for further characterization.

2.2. Scanning electron microscope (SEM)

Microstructural analysis of the films was carried out using a scanning electron microscope (PHENOM Pro). Films were fixed on copper stubs, and gold-coated, and then observed using an accelerating voltage of 5 kV.

2.3. Optical properties

The transparency of the films was determined by using a UV spectrometer (WFZ UV-3802). The transmittance spectra of the films were measured from 200 to 800 nm.

2.4. Dynamic mechanical analysis

A PerkinElmer Pyris Diamond DMA was used to study dynamic mechanical properties of the films. The specimens were cut into 10 mm × 20 mm strips and fixed in a grip probe. The measurements were performed at a constant frequency of 1 Hz from 25 to 150 °C with a heating rate of 2 °C/min. The viscoelastic properties such as storage modulus (E'), loss modulus (E'') and loss tangent ($\tan\delta = E''/E'$) were measured.

2.5. Thermogravimetric analysis (TGA)

Thermal stability of the samples was evaluated using a PerkinElmer Pyris 1 TGA system. Samples were heated from 30 °C to 700 °C at 10 °C/min in nitrogen atmosphere.

2.6. Mechanical characterization

Tensile properties were evaluated in accordance with the ASTM D5938 standard using an Instron tensile testing apparatus (5565). Tensile strength (σ_t), elongation at break (ε_b) and elastic modulus (E) were measured at a crosshead speed of 10 mm/min. All the specimens were equilibrated at 75% RH and 57% RH respectively for three days before testing. Seven specimens were tested for each sample and the mean values were reported.