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

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.

Keywords: A. Hybrid; B. Mechanical properties; B. Physical properties; E. Casting.

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 non-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 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 mPas; 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 hrs. The films were then removed from the dishes and kept under different relative humidity (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.

2.7. Oxygen permeability (OP)

Oxygen transmission rates of the films were measured by Mocon OXTRAN[®] 2/21H Master (MH) and Satellite (SH) systems (Mocon Inc., Minneapolis, MN) according to the ASTM D-3985 standard. The exposure area for testing was 50 cm² for each sample.

3. Results and discussions:

3.1. Microstructural analysis

The final structure of the film depends on both the interactions between film components and drying conditions for film forming, and has a great impact on the different film properties [44, 45]. The inherent gel nature and blend ratio in the blends, affects the morphology, which further influences the surface structure and the properties of the resulting films [24, 46]. In this sense, the

microstructural analysis of the films gives relevant information about the arrangement of the components, which, in turn, help us in understanding the barrier, mechanical or optical properties.

Fig. 1 shows the SEM micrographs of the surfaces of various HPMC/HPS films. Some samples have micro-cracks which could be due to the reduced water content in the samples during SEM testing, or result from the attack of the electron beam in the microscope chamber during the measurement [46, 47]. It is seen that both pure HPS and pure HPMC films had a relatively smooth surface. Pure HPS films showed a more smooth surface and homogeneous microstructure than pure HPMC, possible due to better arrangement of starch macromolecules (amylose and amylopectin) with water during cooling. Different authors reported that there could be a competition between gel formation and phase separation in the amylose-amylopectin-water systems, and, if the rate of phase separation was lower than that of gelation, no phase separation occurred in the system during cooling [48, 49]. Moreover, the phase separation was apparently prevented by amylose gelation and the formation of a continuous amylose network when amylose proportion was higher than 25% [49]. The amylose content in HPS used in this research was 80% (much higher than 25%), which sheds the light on why pure HPS films were more smooth and homogeneous than HPMC.

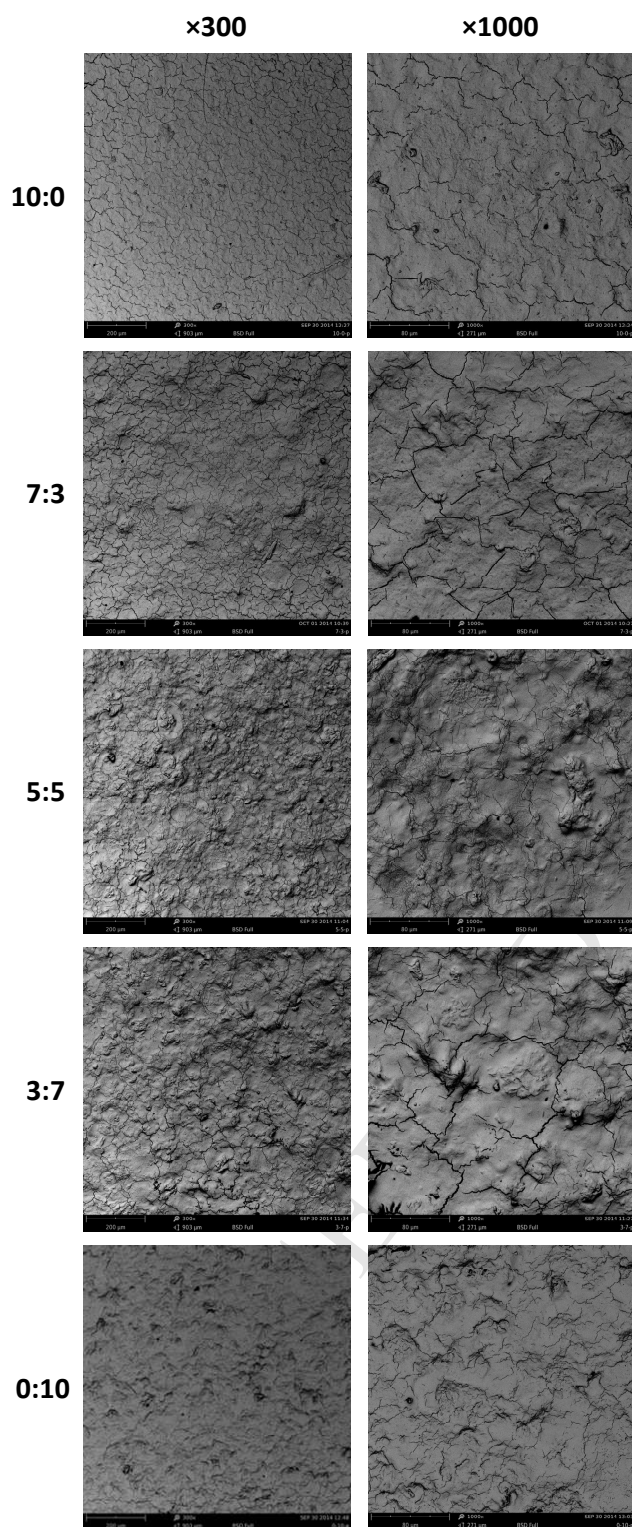


Fig. 1 SEM images of the surfaces of blend films with different HPS/HPMC ratios.

In contrast, a rough surface with irregular bulges was observed for all blend films, meaning some degree of immiscibility between HPMC and HPS. Moreover, blends with high HPMC contents ($\geq 50\%$) showed a more heterogeneous structure than those with high HPS contents. It could be noticed that when the HPS content in the blend was high (7:3 HPS/HPMC), HPS was as a continuous phase with HPMC dispersed in big separate domains. But with a higher HPMC content (lower HPS content), the HPMC domains merged into a continuous phase, while HPS became a dispersed phase. Nevertheless, in all the cases here, there was no clear phase boundary between the two phases, indicating the good compatibility between HPMC and HPS.

3.2. *Optical property*

Fig. 2a shows the transparency of the films with different HPS/HPMC ratios, as indicated by UV transmission. It is seen that all the films showed a similar pattern over the wavelength range in question. The UV transmission (i.e., transparency) firstly increased with the wavelength and then leveled off when the wavelength was greater than 350 nm. The transmission values at 500 nm are presented in Fig. 2b. It can be seen that the transmission for pure HPS was lower than that for pure HPMC, and with the blend ratio changed from 10:0 (pure HPS) to 0:10 (pure HPMC), the transmission was firstly decreased to a lowest value and then increased. It is well known that a homogeneous system generally show better transparency, reflected by a high UV transmission value, while materials with heterogeneous structure is usually more opaque with lower UV transmission. The decrease in UV transmission after blending HPS and HPMC means the blends were more opaque, which might be explained by the phase separation of the two components.

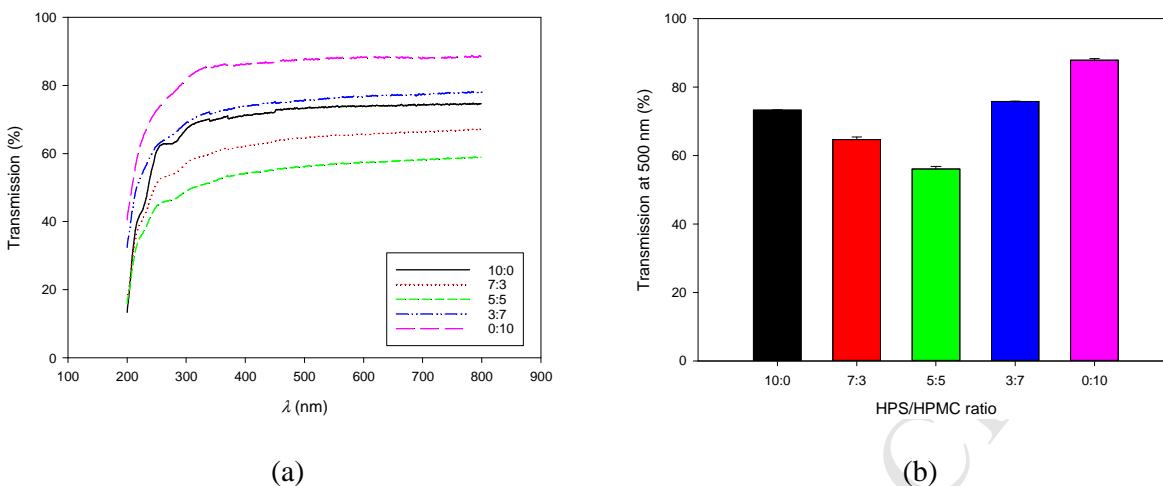


Fig. 2 UV spectra at all wavelengths (a), and at 500 nm (b), for HPS/HPMC blend films.

3.3. Dynamic mechanical analysis (DMA)

Fig. 3 exhibits the temperature dependence of elastic modulus (E') and loss tangent ($\tan \delta$) for various HPS/HPMC films determined by DMA. It can be seen from Fig. 3a that, for the different blends, E' decreased with increasing HPMC content. Besides, for all the samples except pure HPS (10:0), E' decreased continuously as a function of temperature. In contrast, the pure HPS film showed a slight increase after the temperature was higher than 70 °C. For the blend films with high HPMC contents (5:5, 3:7 and 0:10), E' decreased significantly with temperature, while the films containing high HPS contents (10:0 and 7:3) only decreased slightly at high temperatures.

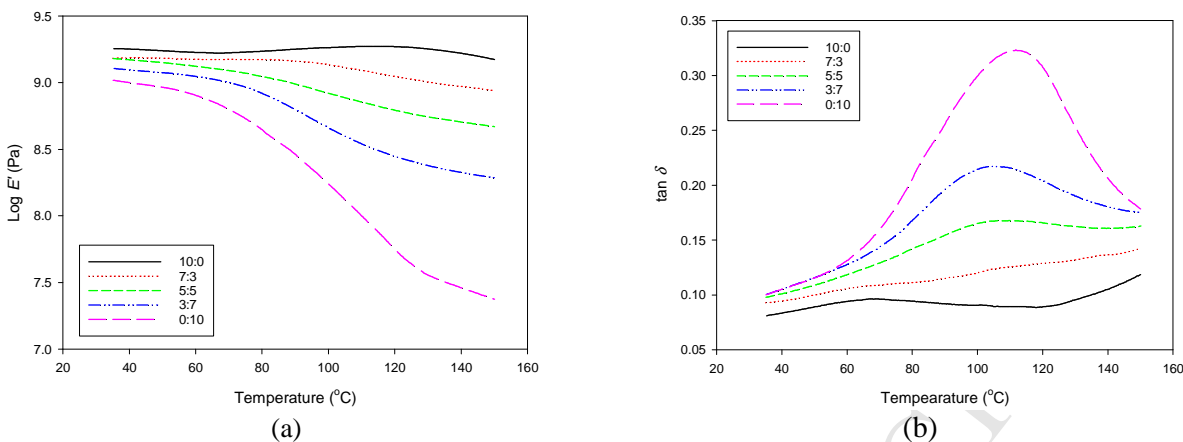


Fig. 3 Storage modulus (E') (a) and loss tangent ($\tan \delta$) (b) of HPS/HPMC blend films.

From Fig. 3b, the HPS/HPMC blend films 5:5, 3:7, and 0:10 showed one main relaxation peak on the $\tan \delta$ curve, which was due to the glass transition. And this transition was slightly shifted to higher temperatures with the increased HPMC content, suggesting the decreased mobility of polymer chains of HPMC. On the other hand, pure HPS had a moderate peak at *ca.* 67 °C. And there were no apparent transitions shown for the 7:3 HPS/HPMC film. It was proposed that there were some degree of interactions (compatibility) between HPS and HPMC which could restrict their segmental motion (thus the glass transitions) of these two polymers.

3.4. Thermal stability

The thermal stability of the films was evaluated by thermogravimetric analysis (TGA) in a temperature range of 30-700 °C and the results are shown in Fig. 4. It can be seen that there was a minor weight loss from 30 °C to 180 °C for all the films, which should result from the moisture evaporation from the materials. After that, a major weight loss occurred between 300 and 400 °C, which was related to the thermal decomposition of HPS and HPMC. It is seen from the derivative

(DTG) curves that the peak for the pure HPS film was at 338 °C while the peak for the pure HPMC film was at 400 °C, indicating that HPMC had higher thermal stability than that of HPS. All the blend samples showed two decomposition peaks representing HPS and HPMC respectively. It is noticed that the film with higher HPS content (7:3) had a peak at 347 °C which was slightly higher than that for pure HPS. In contrast, the film with a high HPMC content (3:7) had a peak at 400 °C which was same as that of pure HPMC. The results suggest that HPMC could improve the thermal stability of HPS to a certain degree, suggesting a certain degree of compatibility between two components.

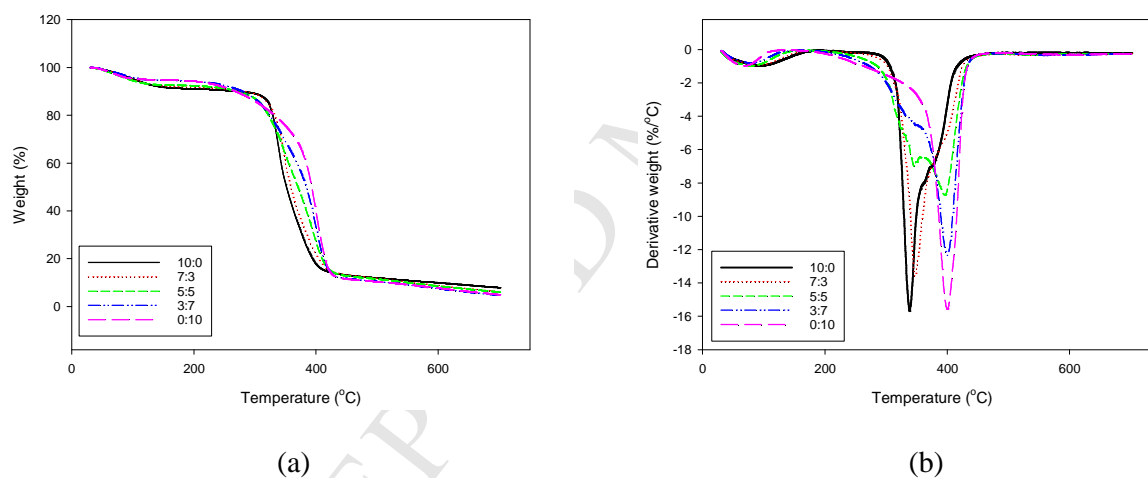


Fig. 4 TGA curves (a) and their derivative (DTG) curves (b) of HPS/HPMC blend films.

3.5. Mechanical properties

The tensile properties of various films were tested at 25 °C after equilibrated at 57% RH and 75% RH conditions, respectively. The results of Young's modulus (E), tensile strength (σ_t) and

elongation at break (ϵ_b) of the films are shown in Fig. 5. It can be seen that at 57% RH, the pure HPS film had the highest E and σ_t , while the pure HPMC film showed lowest values. Generally, both E and σ_t of the HPS/HPMC blend films were increased with a higher HPS content. It can be noted that ϵ_b of the pure HPS film was much lower than that of the pure HPMC film, while both pure films had much higher ϵ_b than those of all blend films. The lower ϵ_b value of the pure HPS film compared to that of pure HPMC film was due to the fact that HPS formed gel during drying which became a rigid structure in the film, resulting in less possibility for the molecules to move. The inter-molecular interactions between HPS and HPMC were higher than intra-molecular interactions within each pure material, which significantly decreased the elasticity of each component. This could also be inferred from the ϵ_b values of blend films which were much lower than that of each pure film.

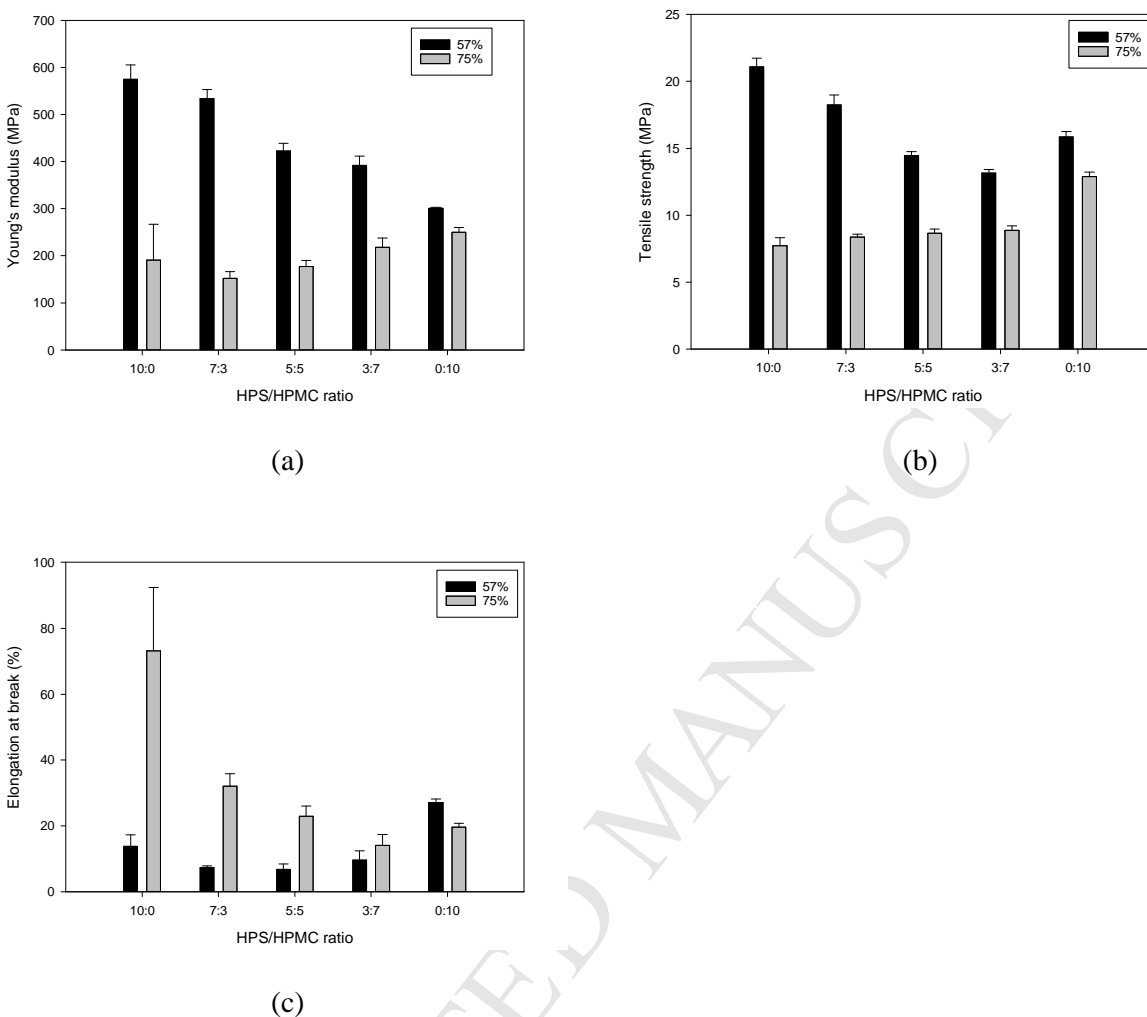


Fig. 5. Tensile properties of HPS/HPMC films with different HPS/HPMC ratios equilibrated under different relative humidity (RH) conditions.

At higher RH condition (75%), E and σ_t were decreased significantly, while ε_b values were generally increased for all the materials. These results are as expected since water could act as a plasticizer for both HPS and HPMC. It is noted that at higher RH, both E and σ_t of the pure HPMC film were higher than those of the pure HPS film, but ε_b was lower for the pure HPMC film. It is important to point out that unlike the results at 57% RH, the results at 75% RH showed an opposite

changing pattern. Regarding this, it was proposed that water not only plasticized the biopolymer matrix, but also favored recrystallization of especially the starch phase (as starch has higher tendency to recrystallization); therefore, water affected HPS more than HPMC.

The mechanical results here could provide a window to obtain optimized mechanical properties for different requirements.

3.6. *Oxygen permeability*

The performance of the blend films as a barrier to the environmental oxygen was analyzed since it is an important characteristic as a packaging material to increase the shelf life of foods. Oxygen permeability (OP) of various films was measured at 23 °C and the results are presented in Fig. 6. It is seen that the oxygen permeability of pure HPS film was significantly lower than that of pure HPMC film, indicating better oxygen barrier property of the starch film. It is speculated, due to the lower viscosity and the amorphous nature, HPMC could form a less dense network in the film, compared to a much compact structure of HPS, which had a higher tendency to recrystallize. Previous studies [24, 46, 50, 51] have also shown that starch films have very good oxygen barrier property compared with other polymers. The oxygen permeability of HPMC film was significantly decreased when HPS was blended in, and was decreased sharply with the increased HPS content. The presence of less impermeable HPS could increase the tortuosity of passage for oxygen in the film, which led to slower oxygen diffusion and, hence, lower oxygen permeability. Similar results have been reported before for raw starches [24, 46].

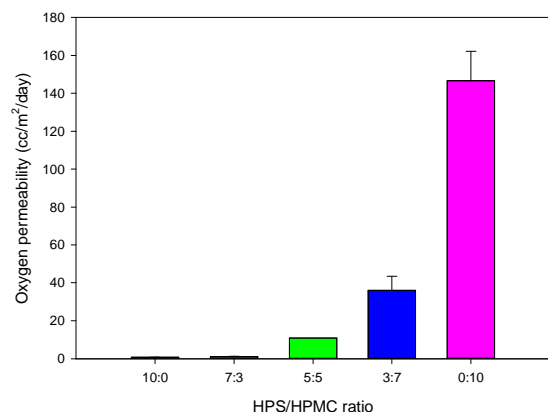


Fig. 6 Oxygen permeability of HPS/HPMC blend films.

4. Conclusion

This work reported novel thermal/cooling-gel bi-phasic systems, in which the morphology and thermal transition can be greatly influenced by the individual thermal (HPMC) and cooling (HPS) gels. Both SEM and DMA indicated the blend system was immiscible but compatible to a certain degree, since there was no observable boundary between the two phases and most of the blend films showed only one relaxation peak. Moreover, associated with the special morphology created by the two phases, the mechanical and oxygen barrier properties of the films could be well tailored by the ratio of two biopolymers and the environmental conditions (RH). Both E and σ_t of blend films were increased with a higher HPS content, while ε_b of all blend film was much lower than that of the pure films at relative low RH (57%) condition. However, at higher environment RH (75%), E and σ_t were decreased significantly, while ε_b values were generally increased for all the materials, and the results of films with different HPS/HPMC ratio showed an opposite changing pattern. There was a cross point of mechanical properties for the films with different blending ratios under different relative humidity conditions, which provide information to obtain optimized mechanical properties for

desired applications. Besides, the increased HPS content could significantly improve the oxygen barrier property of HPMC films due to the less permeable HPS phase in the HPMC matrix.

Therefore, HPS can be used not only to reduce the cost, but also improve the performance, of HPMC films.

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