Relationship between morphologies and mechanical properties of hydroxypropyl methylcellulose/hydroxypropyl starch blends

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A B S T R A C T

Edible films from the blending hydroxypropyl methylcellulose (HPMC) with hydroxypropyl starch (HPS) have been developed. This work focuses on the relationship between morphologies and mechanical properties of such systems. To aid understanding of blend morphology, a new technique used to identify the two phases through dying of the HPS by iodine has been developed, which provided a simple and convenient way to clearly distinguish between HPMC and HPS phases. It was found that the blend system is immiscible and there is phase transition point depending on blending ratio and solution concentration. The lower transparency point of the blend and phase transition reign of HPMC from continuous phase to separated phase correspond with the variation of tensile modulus. The modulus and elongation decreased with increased solution concentration, which is correlatable with the morphologies present, where it was found that the HPMC gradually changed from a continuous phase to a distinct phase.

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1. Introduction

The blending of hydroxypropyl methylcellulose (HPMC) with hydroxypropyl starch (HPS) is of both commercial and scientific importance. From the commercial perspective, blends of HPMC/HPS are of interest in food and medicinal applications. Edible HPMC films are attractive for their ability to assist food to retain its freshness or to reduce the unpleasant odour and taste of medicines. This is due to the fact that HPMC is a readily-available, non-ionic, edible plant derivative which is odourless and tasteless, yet has desirable properties such as transparency, oil-resistance, water-solubility and good mechanical properties of films (Imran, El-Fahmy, Revol-Junelles, & Desobry, 2010; Villalobos, Chanona, Hernandez, Gutiaerrezz, & Chiralt, 2005). However, its greater price limits its broader applications, even when used for higher value medical purposes such as capsules (Zhang, Liu, Yu, Liu et al., 2013; Zhang, Liu, Yu, Shanks, Petinaks, & Liu, 2013; Zhang, Wang et al., 2013; Zhang, Wang, Liu, et al., 2013). In contrast, HPS is a cheaper material already widely used in the food industry (Bertuzzi, Armada, & Gottifredi, 2007; Phan, Debeaufort, Voilley, & Luu, 2009). The reason for HPMC being the more expensive of the pair is that is HPMC has two substituent groups, making the graft processing much more complex (Fatimi, Tassin, Quillard, Axelos, & Weiss, 2008; Fatimi, Tassin, Turczyn, Axelos & Weiss, 2009). Furthermore, the cellulose raw material used for modification is intrinsically more expensive than starch required to produce HPS. It is expected that by using the much lower cost HPS component to replace a proportion of the more expensive HPMC, the overall cost can be reduced whilst maintaining similar functionality, since both are water soluble polysaccharides and comprised of the same glucose chemical unit.

The morphologies and phase transitions of blends of a low temperature gel (HPS) and a thermal gel (HPMC) are dynamic and depend on a number of factors, such as solution concentration, blend ratio, shear stress, temperature and annealing time – the manipulation of all of which can be used to further explore the relationship between the microstructures and properties of such thermal-cool gel blend systems. Furthermore, it is expected that the gelation and rheological properties of the thermal-cool gel system will need to be balanced through blending, especially increasing the viscosity and gel strength of HPMC at lower temperature, which will
improve the processability of HPMC for many applications (Zhang, Wang, Liu et al., 2013, Zhang et al., 2015).

Kadokawa, Murakami, Takegawa, & Kaneko (2009) have shown that a cellulose-starch composite gel has limited compatiblity. Correa, Añón, Pérez, & Ferrero (2010) found that the effect of HPMC on dough stability also depended on the presence or absence of salt. Lorenzo, Zaritzky, & Califano (2009) also showed that dough containing HPMC had good quality. Recently Jimenez, Jose Fabra, Talens & Chiralt (2012) used HPMC to reduce the retrogradation of native starch and to improve permeability of casted starch films. Our previous research (Zhang, Wang, Liu et al., 2013) reported that the hydroxypropyl groups grafted on to both cellulose and starch improve the compatibility between the HPMC and the modified starch.

In this work, the effect of blend ratio, solution concentration on the morphologies, phase transition and tensile properties of HPMC/HPS blends were all systematically investigated. The relationship between the morphology and mechanical properties of HPMC/HPS blends will be established and discussed.

A clear necessity when studying the morphologies and phase diagram of a blend system is to be able to identify each material using a suitable technique. However, it is very difficult to distinguish the two phases of HPMC and HPS since both materials are transparent and do not have sufficient contrast under an optical microscope to differentiate them, and there likewise is no difference in energy absorption between them (both are carbon-based, organic materials) and therefore is not readily distinguished by scanning electron microscopy (SEM), and in any case would have to be dry for such a technique. Fourier Tranform Infrared (FTIR) was a possibility that could be used to map the morphologies and phase image of the protein/starch blends (Zhang, Liu, Yu, Shanks, Petiaks, & Liu, 2013; Liu et al., 2014) based on the ratio of areas of the saccharide bands (1180–953 cm⁻¹) and the amide bands (1750–1483 cm⁻¹), however the technique is very complex and normally needs a synchrotron FTIR technique to produce sufficient contrast. Other complex techniques, such as Cryo-TEM images and SAXS (Bodvik et al., 2010) have also been used. In this work, we have attempted to develop a much simplier drying technique, which allows the different phases to be distinguished under a conventional optical microscope. Based on the fact that the end group of the helix in amyllose containing starch can interact with iodine and form inclusion compounds, we have developed a technique to identify the HPS in the blend by such iodine staining.

2. Materials and methods

2.1. Materials

A commercially-available, pharmaceutical grade of HPMC (HT-E15) from Hopetop Pharmaceutical Company, China, was used in the work (methoxyl content on dry basis is 29%; hydroxypropyl oxygen content on dry basis is 8.4%). A food-grade hydroxypropylated corn starch (A1081) with molar substitution (MS) of 0.11 was supplied by Penford (Australia). Iodine, Potassium Iodide and alcohol (analytical reagent) were bought from Guangdong Guanghua Technology Limited.

2.2. Solution and film preparation

Solutions of 3%, 5%, 7% and 9% HPMC (w/w) were prepared by dispersing the HPMC powder into hot water and reducing the solution to room temperature to dissolve HPMC. Solutions of 3%, 5%, 7% and 9% HPS (w/w) were made by gelatinizing HPS solution at 99 °C for 0.5h, and then rapidly cooling the hot solution to room temperature.

The samples used to investigate the effect of various parameters such as blending ratio, concentration, temperature, shear rate, shear time on the morphology of HPMC/HPS blends were prepared as follows:

2.2.1. Blending ratio

Different ratios of HPMC/HPS (w/w) (100:0, 90:10, 80:20, 70:30, 60:40, 50:50, 49:51, 40:60, 30:70, 20:80, 10:90 and 0:100) solutions in same concentration were mixed at 21 °C, with a blender speed 250 rpm for 30 min. Films were prepared by casting the solutions of different blend ratios on glass and drying them at 21 °C under 53% RH for about 30 min.

![Fig. 1. Photos of films (left) and capsule (right) of samples from HPMC/HPS 70:30 blend.](image-url)