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Developing gelatin–starch blends for use as capsule materials

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ABSTRACT

Blends of gelatin with up to 50% hydroxypropylated high amylose (80%) corn starch were developed as capsule materials. Poly(ethylene glycol) (PEG) was used as both a plasticizer and a compatibilizer in the blends. In order to prepare hard capsules for pharmaceutical applications using the well-established method of dipping stainless steel mold pins into solution, solutions with higher solids concentrations (up to 30%) were developed. The solutions, films and capsules of the different gelatin–starch blends were characterized by viscosity, transparency, tensile testing, water contact angle and SEM. The linear microstructure of the high amylose starch, and the flexible and more hydrophilic hydroxylpropylene groups grafted onto the starch improved the compatibility between the gelatin and starch. SEM revealed a continuous phase of gelatin on the surface of films from all blends. The water contact angle of pure gelatin and the different blends were similar, indicating a continuous phase of gelatin. By optimizing temperature and incubation time to control viscosity, capsules of various blends were successfully developed. PEG increased the transparency and toughness of the various blends.

1. Introduction

Gelatin exhibits good film-forming and gas barrier properties, and it has been used widely in the food and pharmaceutical industries. Gelatin capsules have been developed and used in pharmaceutics since the early 19th century, and the technology has remained essentially unchanged (Jones, 2004b). However, the higher price of raw materials and the well-recognized shortcomings of gelatin capsules, such as animal-derived ingredients, lower soft temperature and the instability of moisture in gelatin, have led to attempts to use replacement substances (Zhang et al., 2013), such as hydroxypropyl methylcellulose cellulose (HPMC) (Al-Tabakha, 2010; Chiwele, Jones, & Podczeck, 2000; Cole, Cadé, & Benameur, 2008; Ku et al., 2010; Ogura, Furuya, & Matsuura, 1998) and modified starch (Eith, Stepto, Wittwer, & Tomka, 1987; Gohil, Podczeck, & Turnbull, 2004; Idrissi, Dumesnil, Michel, & Traisenl, 1991; Stepto, 1997; Vilivalam, Illum, & Iqbal, 2000). Although there are many patents and publications on the developing various substances for capsules, only a few non-gelatin capsule products have recently entered the market. The reasons for the lower commercial success include the higher price of these new products due to requirements for new processing facilities, and/or more complex processing conditions. The current techniques and facilities used for manufacture capsules were based on the gelatin. Therefore, the developments of lower cost gelatin-based blends for capsule production using conventional technology, and overcoming the shortcomings of gelatin products have both scientific and commercial importance.

Starch is a popular food ingredient, and it has good film-forming behavior (Arvanitoyannis, Kalichevsky, Blanshard, & Psomiadou, 1994; Arvanitoyannis, Nakayama, & Aiba, 1998; Arvanitoyannis, Psomiadou, & Nakayama, 1996; Li et al., 2011; Psomiadou, Arvanitoyannis, & Yamamoto, 1996; Xie et al., 2009; Yu & Christie, 2005). Both gelatin and starch have separately been widely used to develop edible films and, for various reasons, developing edible films by blending starch with gelatin has attracted much attention (Abdulmola, Hember, Richardson, & Morris, 1996; Al-Hassan & Norziah, 2012; Arvanitoyannis, Psomiadou, Nakayama, Aiba, & Yamamoto, 1997; Firoozmand, Murray, & Dickinson, 2009; Jagannath, Nanjappa, Das Gupta, & Bawa, 2003; Mousia, Farhat, Blachot, & Mitchell, 2000; Mousia, Farhat, Pearson, Chesters, & Mitchell, 2001; Ong, Whitehouse, Abeysekera, Al-Ruqaie, & Kasapis, 1998). For example, films made of polysaccharides and proteins show better gas barrier (O_2 and CO_2) properties than any pure films (Arvanitoyannis et al., 1994, 1997, 1998; Baldwin, Nisperos-Carriedo, & Baker, 1995). Previous research has shown that gelatin and starch are immiscible and that phase separation affects the rheological, processing and

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mechanical properties of their blends. In most cases, gelatin shows as a continuous phase even in starch-rich blends (Abdulmola et al., 1996; Mousia et al., 2000, 2001). However, their compatibility can be improved by various methods. Firoozmand et al. (2009) found that the time-dependent modulus of gelatin–starch gels was sensitive to the extent of gelatin crosslinking, as influenced by the thermal processing conditions. Under certain processing conditions, a gradual increase in starch content produced gels of lower elastic modulus and increased degree of microscopic phase separation. Jagannath et al. (2003) reported that DSC thermograms of gelatin–starch films based on intense thermal blending showed a single glass transition temperature, indicating the complete molecular miscibility of the components. Ong et al. (1998) found that phase separation depended on pH. Arvanitoyannis et al. (1997, 1998) reported that higher processing temperatures improved the permeability of gelatin–starch films. More recently, Al-Hassan and Norziah (2012) reported that, at a certain concentration, sago starch and fish gelatin could form compatible films.

It is well known (Liu, Yu, Chen, & Li, 2007; Liu, Yu, Liu, et al., 2009; Liu, Yu, Simon, et al., 2009; Whistler, Bemiller, & Paschall, 1984) that starch is a heterogeneous material containing two microstructures: linear (amylose) and branched (amylopectin). Previous studies (Biliaderis, Page, Slade, & Sirett, 1985; Jovanovich & Añón, 1999; Liu, Yu, Liu, et al., 2009; Liu, Yu, Simon, et al., 2009; Raphaelides & Karkalas, 1988) have found that amylose and protein could form an amylose–protein complex, which is stable up to 90 °C in excess water solution. It is expected that this complex will improve the compatibility between gelatin and starch. Furthermore, hydroxypropylation has been widely used to improve the viscosity, transparency and stability of starch products (Lan et al., 2010; Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998; Wurzburg, 1987). It is also expected that the flexible and hydrophilic groups of hydroxypropylene are more compatible with gelatin. Another key property of starch modification by hydroxypropylation is its toxicological safety (Tharanathan, 2005), and so it has been widely used as a food ingredient, as well as being used alone as capsule material (Eith et al., 1987; Gohil et al., 2004; Idrissi et al., 1991; Stepto, 1997; Vilivalam et al., 2000).

The aim of this work was to blend gelatin with hydroxypropylated high amylose (80%) corn starch to develop hard capsule materials. Poly(ethylene glycol) (PEG) was used as both a plasticizer and a compatibilizer in the blends. In order to prepare hard capsules for pharmaceutical applications by the well-established method of dipping mold pins into solution and then drying, solutions with higher solids concentrations (up to 30%) were investigated and developed. Films with different ratios of gelatin/starch were prepared by casting. The viscosity of various solutions was studied by viscometry, and the mechanical properties of the films were studied by tensile testing. The morphologies and compatibility of gelatin and starch were investigated by transparency, SEM and water contact angle.

2. Experimental

2.1. Materials and solution preparation

A commercially available gelatin (GELITA UG719-N, Sweden) was used in this work. A food-grade hydroxypropylated high amylose (80%) corn starch (A1081) with MS (molar substitution) 0.11 was supplied by Penford (Australia). Poly(ethylene glycol) (PEG 400) was purchased from Sigma.

Solutions were prepared using blends of gelatin and hydroxypropylated starch with added plasticizers (water and PEG). Solutions were prepared with different ratios of gelatin and hydroxypropylated starch (100:0, 90:10, 80:20, 70:30, 60:40, 50:50) based on a total weight basis (150 g) including 5% (w/w) PEG in 350 mL distilled water. The mixed materials were dissolved in distilled water at 80 °C for an initial 30 min at a slow stirring speed (100 rpm), then for a further 30 min at high speed (700 rpm) until a clear solution was obtained. A previous study (Lan et al., 2010) showed that the gelatinization of this hydroxypropylated starch occurred at about 57 °C, which is lower than the temperature of solution preparation used in this study.

2.2. Casting films and capsule preparation

After degassing, 50 mL of a solution was poured onto a polyethylene plate (10 cm × 15 cm), which was kept level to control film thickness. The cast film was dried overnight at 37 °C, similar to capsule preparation. The dry films were peeled from the plate, placed in a desiccator containing saturated sodium bromide (NaBr) solution, and stored at 56% RH and 23 °C until required for analysis. Separate control films of pure gelatin and pure starch were prepared in the same way. The weight of the dry films was measured daily until no further measurable weight change was observed, and the thickness of the films was recorded using a micrometer. All films were about 0.3 mm thick with about 8% SD.

Capsules were prepared by dipping stainless steel mold pins (cylindrical, 7 mm diameter) into the solutions and then drying at 37 °C, as described in detail previously (Jones, 2004a). Drying time depended on capsule rigidity, and those containing a higher concentration of starch required a longer drying time, as starch has a stronger hydroxyl bond with water than gelatin. The drying time was increased gradually from 30 to 50 min with increasing starch content from 0 to 50%. Processability was determined by evaluated the viscosity and gelation temperature of the various blends.

An infra-red heating balance (Model DHS-20) was used to measure moisture content in samples through heating samples to 110 °C for 20 min.

2.3. Viscosity measurements

The viscosity of the starch/gelatin solutions was measured at room temperature (23 °C) using a Brookfield digital viscometer (Model DV-II+ PRO with LV S6-3 spindle) operating at 30 rpm for all samples. The viscometer spindle was immersed into the solution for about 3 min to achieve thermal equilibrium between the solution and spindle with continued shearing. Five viscosity readings were recorded for each solution, and average values were taken. Tests were run in triplicate.

2.4. Transparency measurements

A UV (WFZ UV-3802) spectrum was used to measure the transparency of the different solutions, which were placed in a 10 mm × 10 mm square sample container for measurement. A wavelength of 206 nm was used to indicate transparency in this work. The transparency of different films was also measured at a wavelength of 206 nm and divided by thickness and presented as %/mm.

2.5. Mechanical properties

Dumbbell-shaped specimens (gap 50 mm, width 1 mm) were cut from cast films then equilibrated at 56% RH (controlled by NaBr solution) for 72 h before testing. The tensile properties of specimens were measured in accordance with ASTM D638 using an Instron mechanical testing apparatus (Model 3366). Young's modulus, tensile strength and elongation were measured at a crosshead speed of 10 mm/min. Each test trial per film consisted of seven replicate measurements.

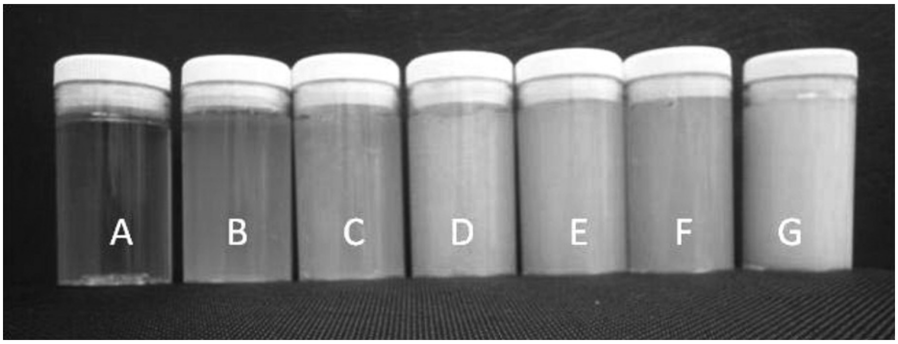

Fig. 1. Photos of the solutions with different gelatin/starch ratios: (A) 100:0; (B) 90:10; (C) 80:20; (D) 70:30; (E) 60:40; (F) 50:50; (G) 0:100.

2.6. Contact angles measurements

The water contact angles of the different films were measured at room temperature (23 °C) using an FTA 200 goniometer (First Ten Angstroms). Measurement was carried out immediately after dropping the water (0.1 mL) onto a sample surface to avoid the effects of receding.

2.7. Scanning electron microscopy (SEM)

A Phillips XL-30 FEGSEM scanning electronic microscope (SEM) was used to investigate the surfaces of the different films. Specimens were first coated with iridium to a thickness of ~0.2 μm in a vacuum evaporator using a Sputter Coater (POLARON SC5750), and subsequently viewed in the SEM at a low accelerating voltage of 2 kV.

3. Results and discussions

3.1. Transparency of solutions

Photographs of the solutions with different gelatin–starch ratios are shown in Fig. 1. No phase separation was observed in the individual solutions. While the pure gelatin solution is reasonably clear, the pure starch solution is cloudy and opaque, due to the retrogradation of starch, which had already been significantly decreased through hydroxypropylation (Lan et al., 2010). The results of the UV spectra measurements of the transparency of the different solutions are shown in Fig. 2, and it is seen that the transparency ratio decreased gradually with increasing starch content. It is noted that the transparency of the pure starch solution was lower than that of all blended solutions, which confirms that the cloudiness of blends is due to starch, and not phase separation. The addition of PEG increased the transparency of the blends, indicating improved compatibility between gelatin and starch.

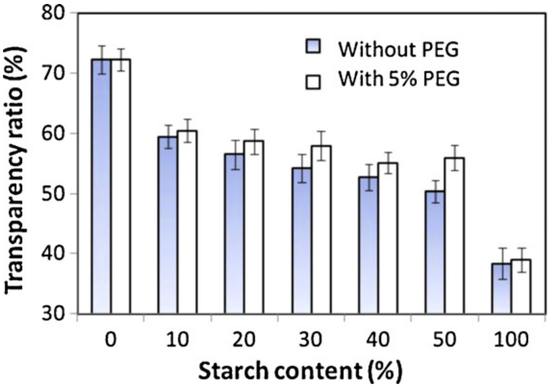

Fig. 2. Transparency of the solutions with different gelatin/starch contents.

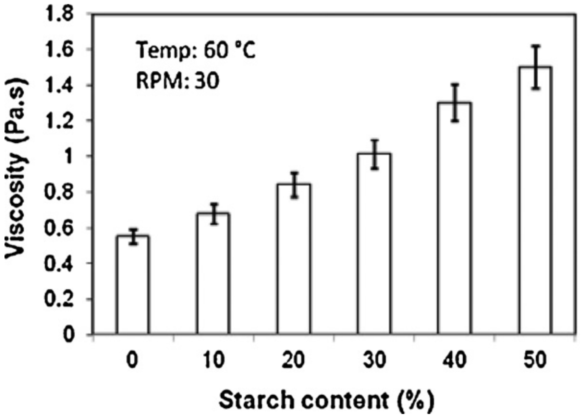

Fig. 3. Viscosity of the various gelatin/starch blends under the same shear rate (30 rpm).

3.2. Viscosity of solutions

Fig. 3 shows the viscosities of the solutions of the different gelatin/starch blends under the same shear rate and at the same temperature. It is seen that viscosity increased significantly with increasing starch content, which is expected since viscosity of the starch solution is much higher than that of gelatin. Gelation temperature, or more particularly the time to the "onset" of gelation, is of critical importance in many applications of gelatin-based materials, including hard capsule manufacture. Despite this, there

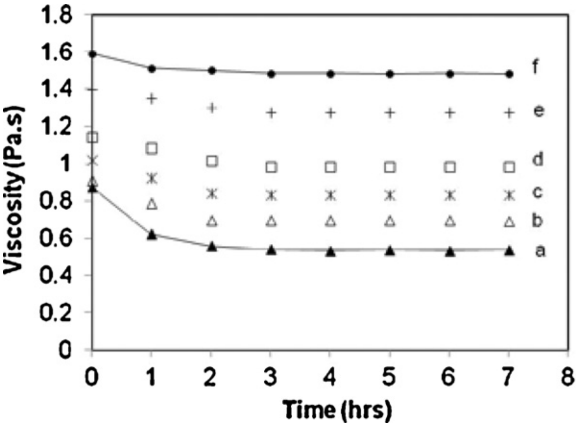

Fig. 4. Effect of incubation time at 60 °C on the viscosity of gelatin/starch blends: (A) 100:0; (B) 90:10; (C) 80:20; (D) 70:30; (E) 60:40; (F) 50:50.

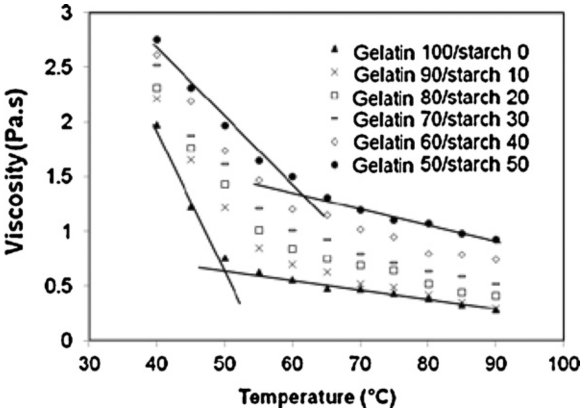

Fig. 5. Effect of temperature on the viscosity of gelatin/starch blends.

is no universally accepted or adopted procedure for measuring the setting time (Jones, 2004b), even though various methods have been developed. These methods are mainly based on detecting either the time at which the viscosity of the solution increases sharply, or a particular degree of rigidity after the setting point has been passed (Jones, 2004a,b). In this work we focused on the effect of temperature and incubation time on viscosity.

Fig. 4 shows the effect of incubation time at 60 °C on the viscosity of the different gelatin–starch blends. The viscosity of the pure gelatin decreased during the first 3 h of incubation then remained stable, as reported previously (Jones, 2004b). For the blended solutions, the decrease ratio with time became less pronounced with increasing starch content, which could be simply explained by the higher viscosity of the solutions containing starch. Fig. 5 shows the effect of temperature on the viscosity of the solutions with different gelatin–starch contents. As expected, the viscosity of all samples increased with decreasing temperature. It should be noted that there is a inflection in the viscosity curve for all samples at about 50–60 °C. This inflection is usually used to indicate the onset of gelation in hard capsule manufacture. The onset temperature can be clearly seen for all blends, although it increased and the slope of the onset became less steep with increasing starch content.

3.3. Properties of capsules and films

Photographs of capsules made from the solutions with different gelatin–starch content are shown in Fig. 6. It is seen that the transparency of the capsules decreased with increasing starch content, corresponding with the transparency of the solutions (see Figs. 1 and 2). Capsule wall thickness increased with increasing starch content under the same dipping conditions, since the starch increased the viscosity of the solutions. In practical terms, the total solids concentration in blended solutions should be decreased with increasing starch concentration to reduce the viscosity.

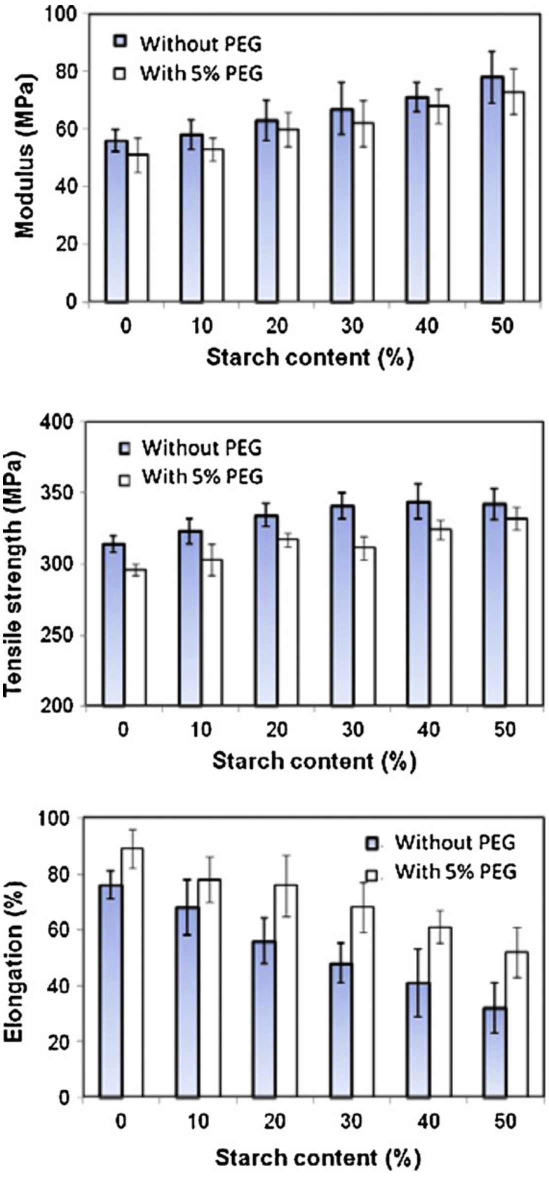

Fig. 7. Mechanical properties of the cast films from different gelatin/starch blends.

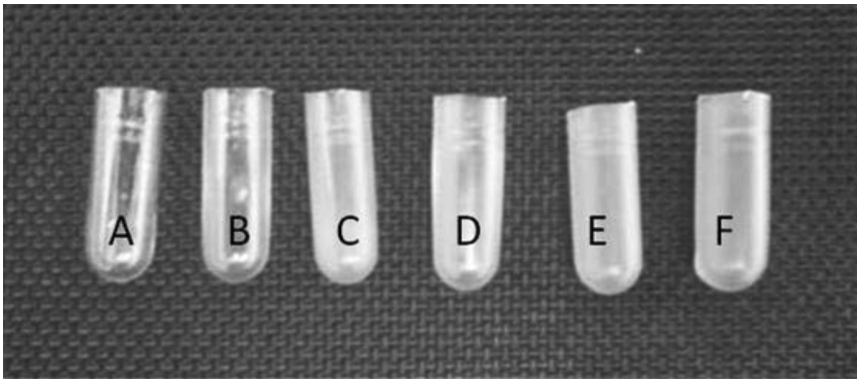

Fig. 6. Photos of capsules made from solutions with different gelatin/starch contents: (A) 100:0; (B) 90:10; (C) 80:20; (D) 70:30; (E) 60:40; (F) 50:50.

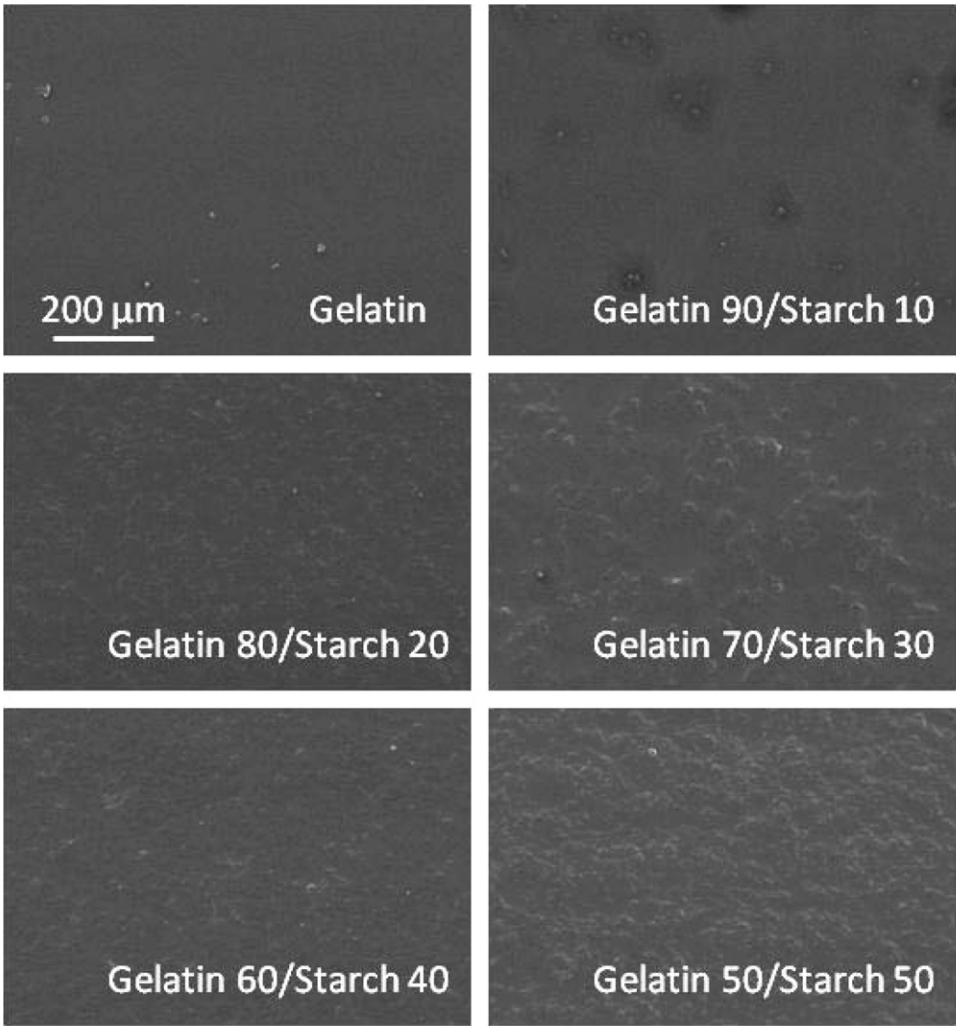

Fig. 8. The film surfaces of various blends observed under SEM.

The mechanical properties of the different films were studied by tensile testing, and the results are shown in Fig. 7. It is seen that the Young's modulus gradually increased with increasing starch content up to 50%. Tensile strength increased slightly, especially for lower starch content films. The elongation of the films gradually decreased with increasing starch content. Generally, the films became more rigid and brittle with increasing starch content after equilibration under the same humidity conditions. Similar results for fish gelatin–sago starch blends have recently been reported by Al-Hassan and Norziah (2012). It is noted that PEG increased the elongation of the blends indicating decreased brittleness.

3.4. *Microstructures and phase composition of different blends*

SEM was used to investigate the microstructures of the surfaces of the films made from the various blends (see Fig. 8). Some protrusions were observed on the surfaces of the films containing starch, and the density of these protrusions increased with increasing starch content. This phenomenon indicates that gelatin and starch are two phases, and that the shrinking ratios of gelatin and starch are different during drying. The individual surfaces are generally present as a continuous phase without indication of phase separation, which means the gelatin and starch are compatible although they are immiscible. Table 1 lists the water contact angles of the different films, and it is seen that the films of pure gelatin and the blends containing up to 50% starch have similar water contact angles. The results indicate that gelatin is a continuous phase, while starch is a separated phase distributed in gelatin and covered by gelatin in all the blends. The starch has smaller water contact angle than gelatin indicating that the starch is more hydrophilic. The better hydrophilic properties guarantee that the blended materials have good water solubility, which is important for capsule materials.

Although phase separation has been widely reported for many gelatin–starch blends, their compatibility can be improved through various processing methods, as previously mentioned. A possible explanation for the improved compatibility found here is the linear microstructure of the high amylose starch, and the flexible and more hydrophilic hydroxypropyl group grafted onto the starch. Using DTA, Arvanitoyannis et al. (1998) have also observed this non-phase separation phenomenon in gelatin–hydroxypropylated potato starch in a low concentration (2–3%) solution. Furthermore, the addition of PEG is expected to improve the compatibility between gelatin and starch, as it can be dissolved well into both (Laohakunjit & Noomhorm, 2004; Li et al., 2011; Ogura et al., 1998). It is well known that the miscibility of an immiscible polymer blend can be improved by a compatibilizer, i.e. any polymeric interfacial agent that facilitates the formation of uniform blends. PEG acted as both a plasticizer and a compatibilizer in the gelatin–starch blends studied here, as indicated by improved transparency and decreased

Table 1
Water content and contact angles of various blends.

	Gelatin/starch ratio						
	100:0	90:10	80:20	70:30	60:40	50:50	0:100
Water content (%)	17.2 ± 2.1	17.5 ± 2.6	17.4 ± 1.9	17.8 ± 2.4	18.1 ± 2.3	17.8 ± 2.1	18.5 ± 2.2
Contact angle (°)	113.7 ± 4.1	111.9 ± 1.6	110.7 ± 1.9	111.3 ± 2.1	107.7 ± 1.8	106.3 ± 3.4	72.3 ± 5.8

brittleness. The compatible microstructure and continuous phase of the blends containing up to 50% starch enabled the production of reasonably good films and capsules. The issue of compatibility and miscibility in this system will be studied in detail in future work.

4. Conclusions

Blends of gelatin and up to 50% hydroxypropylated high amylose corn starch have been developed as hard capsule material. The use of poly(ethylene glycol) (PEG) as both a plasticizer and a compatibilizer increased the transparency and toughness of the various blends. The viscosity of the solutions increased significantly with increasing starch content. The “onset” of gelation temperature was evident for all solutions, and it increased and the slope of onset became less pronounced with increasing starch content.

The linear microstructure of the high amylose starch, and the flexible and more hydrophilic hydroxylpropylene group grafted onto the starch improved the compatibility between the gelatin and starch, even though they are immiscible. The addition of PEG also improved the compatibility between the gelatin and starch, as it dissolves well into both. All film surfaces presented a continuous phase (gelatin) confirming that gelatin and starch are compatible. The compatible microstructure and continuous phase in blends containing up to 50% starch enabled the production of reasonably good films and capsules.

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