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Effect of agar on the microstructure and performance of potato starch film

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ABSTRACT

Films made of agar and potato starch were elaborated and tested for a potential use as food packaging. Fourier-transform infrared spectroscopy (FT-IR) confirmed that starch and agar were compatible and inter-molecular hydrogen bonds existed between them. Scanning electron microscopy (SEM) of composite film with 15% content of agar showed a compact and homogeneous structure. X-ray diffraction (XRD) indicated the composite films were amorphous. At 50% relative humidity (RH), the addition of agar could enhance the tensile strength (TS) from 5.33 to 11.76 MPa. At high moisture environment (75% RH), the addition of agar could also enhance TS value from 0.84 to 3.36 MPa. Fortunately, the addition of 5% agar increased the elongation (E) from 32.5% to 58.33%. Water vapor permeability (WVP) decreased from 6.29 to 4.60×10^{-10} g Pa^{-1} s^{-1} m^{-1}. In conclusion, the addition of agar improved microstructure of starch film, and then meliorated mechanical properties and WVP at high moisture environment. It widened the application of potato starch film in food packaging films as expected.

1. Introduction

Synthetic polymers are important to the packaging industry but most of them are durable and inert or resistant to microbial degradation (Bae, Cha, Whiteside, & Park, 2008), so their use raises aesthetic and environmental concerns, particularly with regard to solid waste accumulation problems and the threat to wildlife (Jayasekara, Harding, Bowater, & Lonergan, 2005). In view of the problems mentioned above, the need for environmentally degradable polymers has increased. Since the 1970s, polar biopolymers such as polysaccharides and proteins have been studied as potential alternatives for synthetic polymers in the film and plastic industries (Garcia, Martino, & Zaritzky, 2000). Among the natural polymers, starch has been considered as one of the most promising candidates for future materials because of attractive combination of price, abundance and thermoplastic behavior (Mali, Grossmann, Garcia, Martino, & Zaritzky, 2005a). Starch is a complex homopolymer of a-D-glucose units which composed of amylose and amylopectin and occurs naturally in plants in the form of granules (Rindlav-Westling & Gatenholm, 2003). Several studies have been done to analyze the properties of starch-based films (Bertuzzi, Castro Vidaurre, Armada, & Gottifredi, 2007; Chang, Abd Karim, & Seow, 2006; Flores, Fama, Rojas, Goyanes, & Gerschenson, 2007; Mali, Grossmann, Garcia, Martino, & Zaritzky, 2006). Unfortunately, there are some strong limitations for developing starch-based products, due to its poor mechanical properties and high moisture sensitivity (Martin, Schwach, Averous, & Couturier, 2001). Cellulose crystallites (Lu, Weng, & Cao, 2006), montmorillonite (Kampeerapappun, Aht-Ong, Pentrakoon, & Srikulkit, 2007), nano-SiO_2 (Tang, Zou, Xiong, & Tang, 2007) have been added to enhance the tensile strength of starch-based films, however, obviously reduction on elongation at break is unavoidable because of the bad compatibility between the additives and starch.

Agar is composed of alternating 1,3-linked-D-galactose and 1,4-linked 3,6- anhydro-L-galactose units. It can be substituted by sulfate esters and methoxyl, and may also carry pyruvic acid residues. Because of its ability to form very hard gels at very low concentrations, agar has been used extensively as a gelling agent in the food industry. Due to its combination of renewability and biodegradability (Freile-Pelegrín, Madera-Santana, Robledo, Veleva, Quintana, & Azamar, 2007), its enormous gelling power, and the simplicity of the extraction process, agar has been singled out as a promising candidate for future use in plastic materials. So far agar has already been made materials such as foams, films and coatings (Lee, Lee, & Song, 1997; Phan, Debeaufort, Luu, & Voilley, 2005), and added into protein films to improve the puncture strength and water vapor permeability (WVP) resistance (Letendre, D'Aprano, Lacroix, Salmieri, & St-Gelais, 2002). However, the effect of agar on the performance of starch films has not been investigated widely.

Plasticizers are added to polymers to reduce brittleness, since they work as spacers between polymer chains, decreasing intermolecular forces and thus increasing flexibility and extensibility of polymers (Romero-Bastida, Bello-Perez, Garcia, Martino, Solorza-Feria, & Zaritzky, 2005). They must be compatible with the film-forming polymers. Hydrophilic compounds such as polyols (glycerol, xylitol, sorbitol, sugar and maltitol) were used in starch

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films (Garcia et al., 2000; Mathew & Dufresne, 2002; Talja, Helen, Roos, & Jouppila, 2007; Teixeira, Da Roz, Carvalho, & Curvelo, 2007). Glycerol was the most suitable plasticizer with respect to mechanical properties and transparency (Mali, Sakanaka, Yamashita, & Grossmann, 2005b; Yang & Paulson, 2000).

The objective of this work is to study the effect of agar on the microstructure and the performance at high moisture environment of starch films with glycerol as the plasticizer. It is expected that the addition of agar could widen the application of starch film in food packaging films.

2. Materials and methods

2.1. Materials

Potato starch (PS, 17% amylose) was obtained from Inner Mongolia Feima Food Company (Hohhot, Inner Mongolia, China). Agar (AG, biochemical grade) was provided by Yingbo biochemical Reagent Factory (Tianjin, China). Glycerol, sodium chloride and potassium chloride (analytical grade) was purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. Methods

2.2.1. Film preparation

A series of agar/starch blends were processed into films by casting method through varying the agar concentration from 0% to 30%. Pure agar films were prepared as a control. Composition of agar and Starch Composite Films are listed in Table 1. They were dispersed in 240 g distilled water, with stirring, and the solution was heated gradually up to 95±5 °C and kept at this temperature for 30 min to form a homogeneous and clear film-forming solution. The film-forming solution was degassed under vacuum to remove dissolved air and then cast into an acrylic mould (18 × 27 cm). After drying in an oven (50 °C) for 10 h, the film was obtained.

2.2.2. Fourier-transform infrared spectroscopy (FT-IR)

Fourier-transform infrared reflection spectra were measured with a BioRad FTS3000 IR Spectrum Scanner (Hercules, CA, USA). Films were tested by the transmission method.

2.2.3. Scanning electron microscopy (SEM)

SEM was used to characterize the micro-structure of the samples. SEM was performed with Microscope Philips XL-3 (FEI Company, Hillsboro, Oregon, USA), operating at an acceleration voltage of 20 kV. Films were frozen in liquid nitrogen and then broken. The fracture faces were coated with gold under vacuum for SEM observation.

2.2.4. X-ray diffraction (XRD)

Films were cut and placed in a sample holder for X-ray diffractometry. X-ray diffraction patterns were recorded in the reflection mode in angular range of 2°–30° (2θ) at the ambient temperature by a BDX3300 diffractometer (Beijing University Instrument Factory, Beijing, China), operated at the CuKα wavelength of 1.542 Å. The radiation from the anode, operating at 36 kV and 20 mA, monochromized with a 15 μm nickel foil. The diffractometer was equipped with 1° divergence slit, a 16 mm beam bask, a 0.2 mm receiving slit, and a 1°-scatter slit. Radiation was detected with a proportional detector.

Table 1
Composition of agar and starch composite films.

Samples	Concentration of agar/% (based on total polymers)	Content of potato starch/g	Content of Agar/g	Content of Glycerol/g
PS	0	8.0	0.0	2.0
PSAG5	5	7.6	0.4	2.0
PSAG10	10	7.2	0.8	2.0
PSAG15	15	6.8	1.2	2.0
PSAG20	20	6.4	1.6	2.0
PSAG25	25	6.0	2.0	2.0
PSAG30	30	5.6	2.4	2.0
AG	100	0.0	8.0	2.0

2.2.5. Water absorption

The films of samples were stored at 75% relative humidity (RH) and 25 °C, for various periods of time, then taken out and weighed immediately. Finally, the samples were cut into small pieces and dried in an oven at 105 °C for 24 h and weighed immediately after being taken out. The water content (K) was calculated as follows:

$$K = (w_t - w_0)/w_0 \tag{1}$$

Here w_t (g) is the mass of the sample stored at 75% RH for every predefined period of time and w_0 (g) is the mass of the dried sample.

2.2.6. Mechanical properties

Tensile strength (σ) and elongation at break (E) of the films were measured using a Testometric AXM350-10KN Materials Testing Machine (The Testometric Company Ltd, Rochdale, UK) operated according to ASTM standard method D882-02 (ASTM, 2002). Tested filmstrips (100 × 15 mm) were cut from each conditioned samples (at 50% RH and 75% RH, respectively, 25 °C) and tested. The thickness of each specimen was measured in five points along its length and averaged. Crosshead speed was set to 50 mm/min. The mechanical properties of five specimens from each sample were measured, and the results averaged.

$$\sigma = \mathrm{F/S} \tag{2}$$

$$\mathrm{E} = \mathrm{L\text{-}L_0/L_0} \times 100\% \tag{3}$$

σ (MPa), tensile strength; F (N), maximum load; S ($\mathrm{mm^2}$), original minimum crosssectional area; E (%), elongation at break; $\mathrm{L_0}$ (mm), the initial gage length; L (mm), the extension at the moment of rupture.

2.2.7. Water vapor permeability (WVP)

Experiments were conducted according to the method of Mali (Mali, Grossmann, Garcia, Martino, & Zaritzky, 2002). Each film sample was sealed over a circular opening permeation cell that was stored at 25 °C in a dessicator. To maintain a 75% RH gradient across the film, anhydrous calcium chloride (0% RH) was placed inside the cell and a saturated sodium chloride solution (75% RH) was placed in the dessicator. The RH inside the cell was always lower than the outside, and water vapor transport was determined from the weight gain of the permeation cell. After steady state conditions were reached (about 2 h), eight weight measurements were made over 24 h. Changes in the weight of the cell were recorded to the nearest 0.0001 g and plotted as a function of time. The slope of each line was calculated by linear regression ($r^2 > 0.99$) and the water vapor transmission rate (WVTR) was calculated from the slope of the straight line (g/s) divided by the cell area ($\mathrm{m^2}$). After the permeation tests, film thickness was measured and WVP ($\mathrm{g\,Pa^{-1}\,s^{-1}\,m^{-1}}$) was calculated as WVP = $[\mathrm{WVTR}/S\ (R_1 - R_2)]d$; where S is the saturation vapor pressure of water (Pa) at the test temperature (25 °C), R_1, the RH in the dessicator, R_2, the RH in the permeation cell and d is the film thickness (m). Under these conditions, the driving force $[S\ (R_1 - R_2)]$ was 1753.55 Pa. WVP of five specimens from each sample were measured, and the results averaged.

3. Results and discussion

3.1. FT-IR

Fig. 1 shows the FT-IR data of nature potato starch (NPS), nature agar (NAG) and plasticized films. The NPS spectrum (a) was similar to the NAG spectrum (b) at the range from 4000 to 2000 cm^{-1}. They had same extremely broad bands from 3100 to 3700 cm^{-1} which were attributed to the complex vibrational stretches associated with free, inter- and intra-molecular hydroxyl groups. Bands at 2925 (a) and 2926 cm^{-1} (b) were respectively characteristic of C–H stretches associated with the ring methine hydrogen atoms of NPS and NAG. The peak at 1640 cm^{-1} (a) was a feature of tightly bound water present in the NPS. However, the peak in NAG (b) at 1640 cm^{-1} was caused by stretching of the conjugated peptide bond formed by amine (NH) and acetone (CO) groups. More differences were found in the fingerprint region. In NPS spectrum (a), three characteristic peaks appeared between 933 and 1156 cm^{-1}; these peaks were attributed to C–O bond stretching. The peaks at 1081 and 1023 cm^{-1} were characteristic of the anhydro-glucose ring C–O stretch (Fang, Fowler, Tomkinson, & Hill, 2002). In NAG spectrum (b), the peak at 1371 cm^{-1} was associated with ester sulfate. Characteristics bands at 1075, 1039 and 930 cm^{-1} attributed to the C–O of 3, 6-anhydro-galactose, and at 886 cm^{-1} were associated with the C–H of residual carbons of β-galactose (Freile-Pelegrín et al., 2007).

The analysis of FT-IR spectra of the composites enabled the interactions to be identified. If there were appreciable band shifts in the FT-IR spectra of the composites with respect to the addition of each component, a distinct chemical interaction (hydrogen-bonding) existed between the components. The lower the peak frequency was, the stronger the interaction was (Ma, Yu, He, & Wang, 2007). As glycerol added, the peaks at 3405, 1158, 1081 and 1023 cm^{-1} in NPS (a) shifted to lower frequency, 3295, 1150, 1078 and 1015 cm^{-1} in PS (c) respectively. Thus, hydrogen bonds between starch and glycerol were stronger than inter- and intra-starch molecules. Similar changes could be observed in NAG (b) and AG (f). On the other hand, the frequency of both O–H and C–O peaks in PSAG15 (d) and PSAG30 (e) were lower than PS (c) and AG (f). It indicated that there were the interaction between starch and agar, which could improve the compatibility of them.

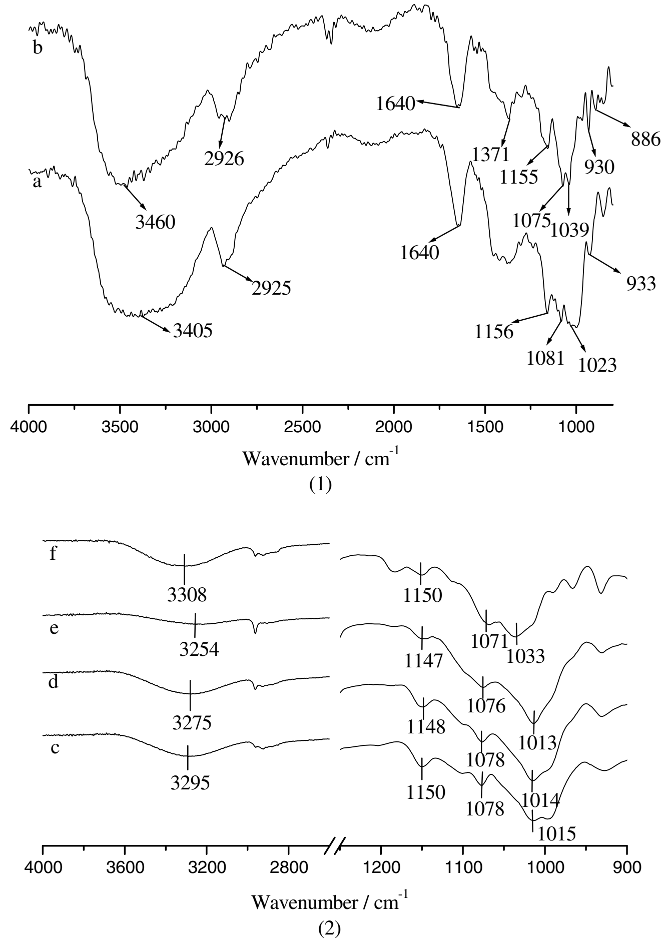

Fig. 1. FTIR spectra of samples: NPS (a), NAG (b), PS (c), PSAG15 (d), PSAG30 (e), AG (f).

3.2. Microstructure observations

Scanning electron micrographs of NPS granules and fractured surface of PS, AG, PSAG15 and PSAG30 films are shown in Fig. 2. NPS granules showed ovate shapes and its surface was smooth. Glycerol is known to enter polysaccharides chain interior, disrupted inter- and intra-molecular hydrogen bonds and made the polymer plastic, forming a continuous phase of plasticized film (Mali et al., 2005b). PS and AG films were all plasticized. The fracture surface of PS film was smoother than AG film. With the addition of agar, PSAG15 film showed a relatively smooth and continuous cross section without any phase separation, which confirmed a homogeneous and dense structure. This may be a result of the intense interaction between starch and agar indicated by FT-IR spectra and the formation of compact agar gel mentioned in Phan's study (Phan et al., 2005). Unfortunately, when more agar was added, the fracture surface was not homogeneous like PSAG15. It may be due to the compatibility of starch and agar was declined when a suitable starch/agar ratio was exceeded (Phan, Debeaufort, Voilley, & Luu, 2008). Therefore, cross section of PSAG30 film was not smooth any more, and showed a multilaminar structure with fine pores and cracks.

3.3. X-ray diffraction

X-ray diffraction patterns of NPS, NAG, PS, AG, PSAG15 and PSAG30 stored for 2 weeks in 50% RH are shown in Fig. 3. NPS was in semicrystalline granules. The pattern of NPS (a) could be assigned to a B type, characteristic of some starch tubers (van Soest, Hulleman, de Wit, & Vliegenthart, 1996). The pattern for NAG (b) showed a peak at 19.09° and a slight shoulder at 14.03° which was consistent with Freile-Pelegrín's study (Freile-Pelegrín et al., 2007). In the process of gelatinization, double helical conformations which formed B-type crystal lattices of NPS was disrupted and the addition of glycerol prevented its comeback. So PS film (c) exhibited an amorphous character. During drying of the film-forming solution, part of agar chains formed double helical conformations due to the inter-molecular hydrogen bonds, which could lead to a strong three-dimensional network structure (Phan et al., 2005). So the pattern of AG was slightly crystalline. PSAG15 (d) and PSAG30 (e) showed similar amorphous patterns to the plasticized starch films. It indicated that the addition of agar in the film formulation did not influence the amorphous character of the composite films.

3.4. Moisture absorption

Moisture absorption is an important index of the sensitivity of material to moisture. Moisture adsorption curves at 25 °C of agar film, starch film and composite films are shown in Fig. 4. Moisture adsorption was more rapid at the initial stages of the storage and lower amounts of water were adsorbed as time increased. Then,

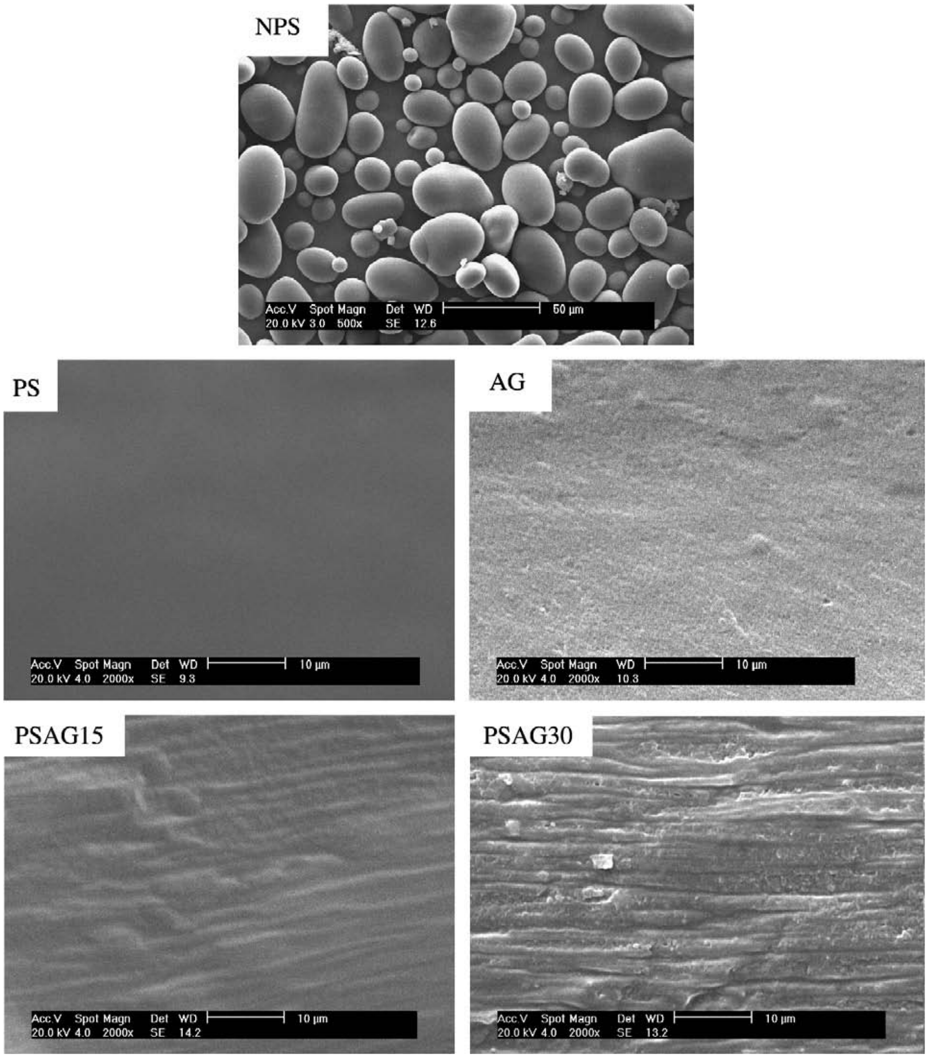

Fig. 2. SEM images of NPS and fracture surfaces of PS, AG, PSAG15 and PSAG30.

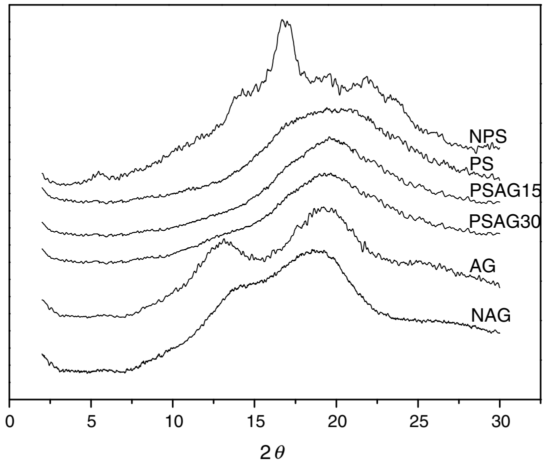

Fig. 3. XRD patterns of samples: NPS, NAG, PS, AG, PSAG15 and PSAG30.

the moisture content of films reached a plateau indicating that they became equilibrated with storage RH. Starch film had the lowest moisture content and agar film had the highest one. When the addition of agar increased, a tendency to increased sorption of moisture had been observed. Characteristically, agar was sulfated polysaccharide. The presence of charged groups resulted in more extended chains with a higher hydrophilicity (Phan et al., 2008). So the presence of agar in the formulation, which was more hydrophilic than starch, increased the hygroscopic characteristics of the films.

3.5. Mechanical properties

After stored at 50% RH for 48 h, the tensile properties of the samples were tested. The tensile strength and elongation at break of the starch film, agar film and starch/agar composite films with the different agar contents are shown in Fig. 5. With the increasing of agar, the TS value of the composite films kept rising and between the value of starch film and agar film. The increase was attributable to the formation of inter-molecular hydrogen bonds between starch and agar and the compact structure of composite film indicated by FT-IR and SEM. Domains of the three-dimensional network structure formed by entanglement among agar chains were increased along with the increasing concentration of agar (Moritaka, 2002). It enhanced the TS of composite films directly. The E values of the composite films first increased with the addition of agar, and reached the maximum 58.33% at the 5% content of agar. At the higher agar contents, the E values of the composite films decreased with further increases in the agar content up to 30%. The

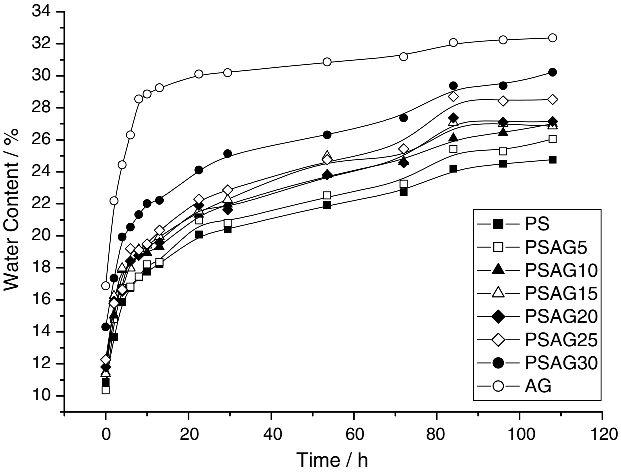

Fig. 4. Effect of agar (AG) content and storage time at 75% RH on the moisture content of composite films.

addition of agar played two roles. The one was absorption and keep of moisture which increased the moisture content of the films. Water was a plasticizer like glycerol (Chang et al., 2006). It would destroy inter-molecular hydrogen bonds between polysaccharide chains and enhance their mobility and then increased E value. The other one was the formation of inter-molecular hydrogen bonds with starch and three-dimensional network structure which restrained the mobility of polysaccharide chains and then decreased E value. At lower concentration of agar, the former predominated. At higher concentration of agar, the later predominated.

Starch and agar were all hydrophilic polysaccharides, so relative humidity 75% was chosen to conditioning the experimental films in order to evaluate the material performance in high moisture content environment. As shown in Fig. 6, compared to the samples stored at 50% RH, the TS values of all the films stored at 75% RH were declined and the E values were increased due to the hydrophilic character of starch and agar. TS of potato starch films fell dramatically from 5.33 to 0.84 MPa and agar film merely from 12.5 to 8.86 MPa owing to the strong three-dimensional network structure (Phan et al., 2005). When the content of agar increased from 0% to 15%, the TS values of the composite increased from 0.84 to 3.36 MPa, and then decreased with further addition of agar up to 30%. The increase was related to the strong interaction between starch and agar chains and the dense structure mentioned above. The decrease in TS with the increasing of agar content from 15% to 30% was caused by the plastic effect of water and magnification of pores and cracks causing by film swelling in higher moisture environment (Bertuzzi et al., 2007). Plastic effect of water to films was enhanced at 75% RH. So the influence of agar content (from 0% to 15%) on E values (73.65%–70.84%) of the composite films was not obvious. When the content of agar exceeded 15%, the decrease became obvious due to the defects in microstructure of films.

Based on the data above, the addition of agar could enhance the tensile strength of potato starch film in both normal and high moisture environment. This could expand the application of potato starch film in food packaging films.

3.6. Water vapor permeability

Water vapor permeability (WVP) of film is an important property that greatly influences the utility of the film in food systems. As shown in Fig. 7, although agar film was more hydrophilic than starch film, WVP of agar film was lower than starch film due to its dense three-dimensional network structure. Addition of 5% or 10% agar gave a marked reduction in the permeability of the film. This would improve the suitability of the composite film for use as a food packaging film, especially in a highly humid environment. However, the further increasing of agar gave no further reduction in permeability. Differences in permeability could be attributed to alterations in film microstructure. When agar was added, strong inter-molecular interaction (cohesion) was formed between potato starch and agar. It minimized free volume and inter-molecular distance in the films. Consequently, water molecules diffused more difficultly in the compact network and the lower WVP value resulted (Phan et al., 2005). However, the effect was not apparent above 15% agar, because of density fluctuations where pores and cracks might be present, which facilitated water vapor permeation.

4. Conclusions

Different from other polysaccharide, agar could form a three-dimensional network gel in the combination which could result in dense film when the moisture vaporized. So agar was chosen to be added into the potato starch films and tested for a potential use as food packaging. The results showed that agar and potato

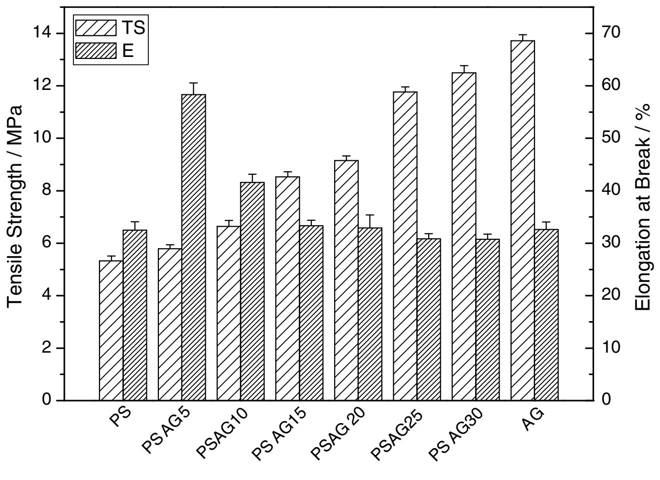

Fig. 5. Effect of agar (AG) content on the tensile strength and elongation at break of composite films stored at 50% RH for 48 h.

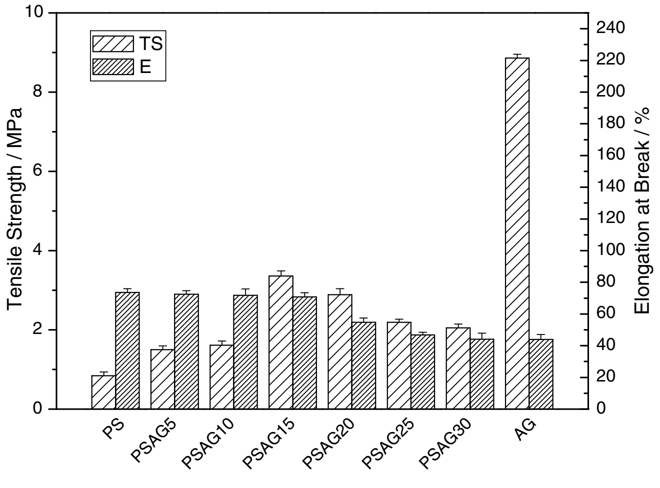

Fig. 6. Effect of agar (AG) content on the tensile strength and elongation at break of composite films stored at 75% RH for 36 h.

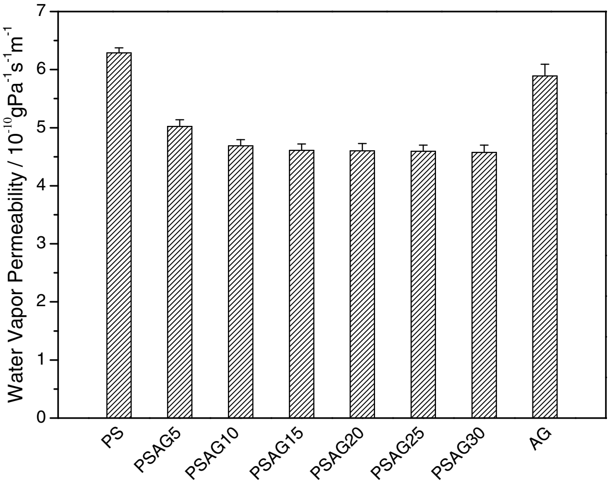

Fig. 7. Effect of agar (AG) content on water vapor permeability of the composite films.

starch were compatible and the addition of agar improved the microstructure of starch film, and then meliorated mechanical properties and WVP at high moisture environment. In present study, the addition of agar could restrain the mobility of starch chains. It was hypothesized that the effect of restrain could prevent the retrogradation of starch film. Therefore, aging experiments would be done in the later. In order to know the influence of starch types on the enhancement of agar, different starches would also be introduced in the future study.

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