Heat-Sealing Properties of Soy Protein Isolate/Polyvinyl Alcohol Film Made Compatible by Glycerol

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ABSTRACT: Heat-sealing properties are necessary for packaging materials. Soy protein isolate/polyvinyl alcohol (SPI/PVA) blend film is a biodegradable potential packaging material. We analyzed the effects of PVA content (0–20%), glycerol content (1–3%), and sealing temperature (180–230°C) on the heat-sealing properties of SPI/PVA blend film. Results showed that SPI/PVA film obtained the desired sealing properties when the PVA content exceeded 15%. The sealing strength increased with the PVA content, reaching a maximum upon blending with 20% PVA and 1% glycerol at 220°C. The temperature at sealing strength was approximately twice that at 180°C. However, glycerol migrated to the surface and hindered the entanglement of macromolecular chains in the sealing interface, thereby resulting in reduction of seal strength. Glycerol vaporization at 204°C led to aesthetically unacceptable blistering in the sealing area. Therefore, the optimum sealing temperature of the blended film was ~200°C. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40308.

INTRODUCTION

Soy protein isolate (SPI), a biopolymer, has attracted considerable research interest in fabrication of soy protein-based biodegradable and edible packaging films, because of excellent film-forming properties, good biodegradability, and low manufacturing costs. Studies on SPI films mostly focus on the modification of the mechanical properties, moisture sensitivity, and packaging characteristics, such as barrier properties and heat-sealing properties.[1–3]

SPI film usage is limited by insufficient mechanical properties and relatively high moisture sensitivity. Currently, commercially significant modification methods to rectify these problems are unavailable. SPI films can be produced as an inner bag that, when combined with a large, high-strength, relatively impermeable, and resealable outer bag, can protect the weaker inner SPI film bag. The heat-sealing properties of SPI films are significant. Heat sealing is more versatile than other sealing methods such as mechanical fastening, adhesive application, ultrasonic sealing, and high-frequency sealing because heat sealing has additional advantages that include safety, convenience, increased productivity, and conferred mechanical strength.[4]

Heat sealing of a thermoplastic material refers to a process by which sufficient heating of films under specific temperature and pressure results in interdiffusion of polymer-chain segments across the interface and creation of molecular entanglements, which are followed by cooling, crystallization, and yielding of a heat-sealed joint.[5]

Seal strength, a main parameter that determines the heat seal quality, is defined as the force per unit width of the seal required to progressively separate the seal under specific test conditions. It depends on jaw temperature (sealing temperature), sealing pressure, and dwell time (i.e., the time spent in the seal cycle when two polymer films are held together by the seal jaws).[6,7]

During the heat-sealing process, the sealing film interface is subjected to viscous flow after melting.[5] The jaw temperature should be set slightly higher than the final melting temperature of the film, whereas the dwell time should be prolonged to allow the interfacial temperature to approach the jaw temperature within a few degrees.[8] Under certain temperature and pressure conditions, prolonged dwell time causes aesthetic unacceptability of the seal and failure to improve seal strength.

Sealing pressure is required for close contact across a significant fraction of the film surface, particularly when two microscopically uneven and heated surfaces are brought together.[8] In case of extremely low sealing pressure, two layers of material are

unlikely to form a seal, which results in a partial weld leakage because of the difficulty in excluding the gas from the weld. Excessive sealing pressures result in rapid heating, wherein the molten material can easily be squeezed out of the weld by the seal jaw. Inevitable extension of pressure leads to heat cutting, which decreases the effectiveness of seal strength. Generally, sealing pressure is positively correlated to the thickness and the width of the film, as well as influences the appearance and strength of the seal. The sealing pressure should be as low as possible and consistent with the requirements of seal formation to minimize seal distortion.

Studies on the heat-sealing performance of edible, biodegradable films, and protein-made coatings have proposed successful heat-sealing methods.[9] Kim and Ustunol,[10] Cagri et al.,[11] and Hernandez-Izquierdo and Krochta[12] analyzed the heat-sealing properties, methods, and processes of whey protein films, and found that these films prepared by both solution casting and extrusion can be heat-sealed by conventional heat sealing or impulse sealing. Shao et al.[13] pointed out that soy protein coating yielded heat-sealable and edible celery paper, but the seal strength was not high. Su et al.[14] examined the heat-sealing properties of SPI/PVA blend films using X-ray diffraction, Fourier transform infrared spectrometry, scanning electron microscopy, and differential scanning calorimetry (DSC), mainly focused on the sealing temperature. Considering merely the sealing temperature is insufficient in studying the heat-sealing performance of new materials.

Pure SPI film is a poor heat-sealable material; thus, modification is necessary to improve the heat-sealing properties of SPI-based degradable films. Plasticized modification is the most common physical method of modifying SPI films. Hydrosoluble and polyhydroxy PVA with good heat-sealing properties can enhance the mechanical strength and heat-sealing properties of blended films. Glycerol is the most common plasticizer for SPI and PVA.[15] The heat-sealing properties of SPI films fabricated via solution-casting method were improved using PVA as a plasticizer and glycerol as an agent to improve compatibility. The effects of PVA and glycerol on the heat-sealability of blended film were studied, and parameters such as sealing temperature, pressure, and dwell time were analyzed.

EXPERIMENTAL

Materials
ISP with a protein content of 90.51% (Wonderful Industrial Group, Shandong, China), polyvinyl alcohol (PVA) (AH-26) with alcoholysis 97–98.8 mol % (Sinopharm Chemical Reagents, Shanghai, China), and glycerol (Guangzhou Chemical Reagents, Guangdong, China) were used.

Preparation of Soy Protein Film
In this study, S-x-1, S-x-2, and S-x-3 series of SPI/PVA blend films with respective glycerol contents of 1%, 2%, and 3% were prepared, where x ($x = 0, 5, 10, 15,$ and 20) was the PVA content. Taking the S-x-2 series as an example, we prepared an SPI/PVA blend film as follows.[16] A weighed amount of PVA, which was added to 10 g of deionized water, was dissolved completely and stirred at 90°C for 60 min. Then, 5 g of isolated soy protein
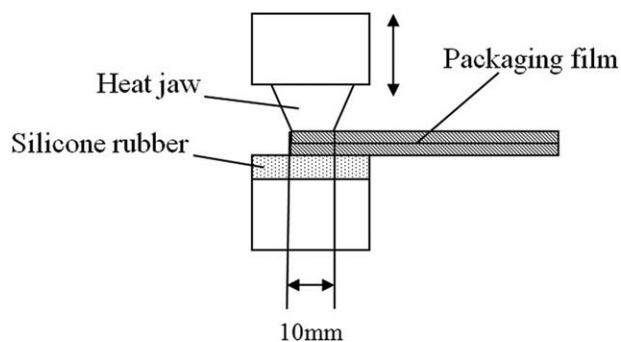

Figure 1. Schematic of heat sealer configuration.

and 2 g of glycerol were added to 90 g of deionized water, mixed, and stirred with a magnetic stirrer for 30 min. PVA solution was poured into the soy protein mixture, and the mixture was stirred for 30 min; pH of the mixture was adjusted to 10 using 1 mol/L NaOH solution and monitored with an electronic pH meter (pHs-25, Hongyi Instrument, Shanghai, China). The mixed solution was placed in a water bath maintained at 50°C and stirred for 30 min. Before the mixture was cooled to room temperature, the treated solution was vacuum-filtrated for 15 min. Then, 50 g of the solution from the previous step was poured into a horizontal Plexiglass box to yield a film through a casting method. The resultant film was fully dried in an infrared oven at 50°C for 24 h, and the glass box was peeled off afterwards. Drying the flipside of the film continued at 50°C for 12 h with the original face oriented downward. The SPI/PVA blended films were stored at a temperature of (23 ± 2)°C and a relative humidity of (50 ± 10)%.

Seal Strength Determination
The sealing strength of SPI/PVA blended films was measured according to QB/T 2358–1998. The films were conditioned in a constant-temperature humidity chamber set to (23 ± 2)°C and (50 ± 10)% RH for over 4 h to adjust the moisture content according to GB/T 2918–1998. The tests were conducted in the same environment.

A heat-seal tester (HST-H3, Labthink Instruments, Jinan, China) was used in the heat-sealing process. Figure 1 illustrates the experimental setup and shows the relative positions of the jaws and film samples. The blended film was positioned between the two jaws, and the footswitch was immediately pressed to lower the upper jaw, resulting in seal[7] formation. The upper jaw was held against the lower jaw at a constant pressure for a preset dwell time, after which the upper jaw returned automatically to the home position. The sealed film specimen was removed and cooled to room temperature. In this process, the sealing temperature was the preset upper jaw temperature but not the actual temperature inside the sealed part when the effects of heat transfer lag in the polymer are considered.[17]

The sealed sample was cut to (15 ± 0.1) mm width and (100 ± 1) mm unfolding length with the heat-sealed part at its centre (see Figure 2). The seal strength was measured through an unsupported T-peel test using an auto tensile tester (XLW (PC), Labthink Instruments, Jinan, China) at a (300 ± 20) mm/min
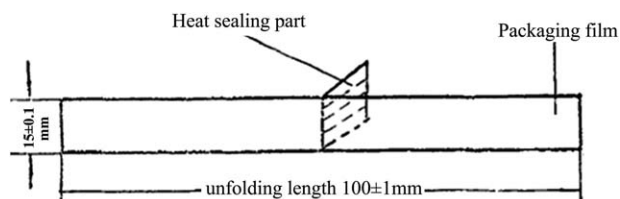
Figure 2. Illustration of seal strength testing samples.

crosshead speed, and an initial grip separation of 50 mm. Seal strength values were reported as the average of three measurements in units of N/15 mm. The failure modes of the test samples were also analyzed.

Seal Failure Modes

The failure modes of the test samples were examined to understand the different seal strength properties. Seven failure modes in ASTM 1921-98 were found (see Figure 3). However, only three failure modes were identified, namely, separation, mode A (seal adhesive peeling), and mode D (material breaking), as shown in Figure 4.

Separation is characterized by complete peeling between films, without damage on the interface between the films, and negligible sealing strength brought by the molten fluid on the interface of the seal beginning to flow together. The polymer layers were not observed when strong inter-layer engagement occurred because of the strong residual molecular orientation in the polymer. The two polymer layers slip and cause unstable interfacial flow; a sealing effect is generated, but with limited strength.[18] The mode of separation indicates insufficient sealing, that is, chain entanglement deficiencies result in weak seals, and the adhesive strength that acts on the sealing area is less than the cohesive strength of the material being tested.[7] Limited elongation was observed among the identified film samples in this failure mode.

Mode A is characterized by complete seal peeling, with varying extents of distortion or breakage on the interface between the separated films. When heat-sealed under pressure, the molten fluid on the interface flows for a sufficiently long time and the interface disappears. The convergence of two molten fluids leads

Figure 4. Three failure modes observed, from left to right, are separation, mode A (peeling), and mode D (breaking). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to interface fitting, and surface molecules are entangled within a layer 18. The cooled, recrystallized new layer leads to high seal strength and a successful heat seal. In this failure mode, the adhesive strength acting on the sealing area has approached the cohesive strength of the test material, resulting in elongation of the samples identified after peel-off.

Mode D is indicated wherein one side of the film on sealed samples is pulled off and breaks at the edge of the sealed area without damaging the sealing interface because the cohesive strength of the new layer formed by entanglements of the interface molecules is greater than the original cohesive force on the film material. Failure occurs at the seal edge in the peeling process because of stress concentration. The tensile breaking strength is obtained instead of the heat-sealing strength, indicating an excessive amount of heat-seal strength. Usage of lower sealing parameter value is recommended. In this failure mode, maximum elongation arises, and wrinkling or heat cutting often occurs at the seal area in mode D, which damages the seal appearance.

DSC Analysis

A differential scanning calorimeter (Q200, TA Instruments, New Castle, DE) was used to determine T_g, T_m, and the heat of fusion (H_f) of the SPI/PVA blended films: 10–11 mg of sample were sealed in DSC pans and heated from 50°C to 300°C at
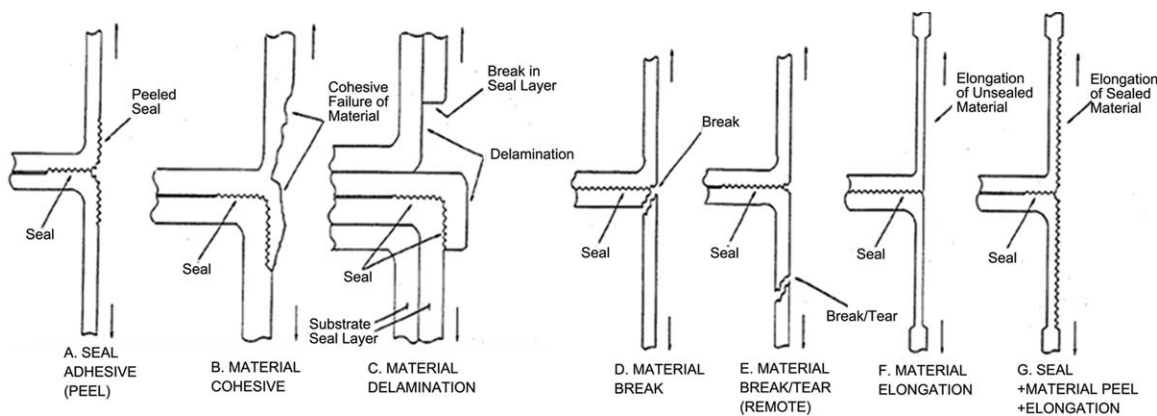

Figure 3. Test strip failure modes. Mode A is seal-adhesive (peel), mode B is material-cohesive, mode C is material delamination, mode D is material break, mode E is material break/tear (remote), mode F is material elongation, and mode G is seal and material peel with elongation.

Table I. T_g and T_m of SPI/PVA Blends Film with Different Content PVA and 1% Glycerol

PVA contant (wt %)	T_g (°C)	T_m (°C)
0	136.5	157.4
5	129.8	158.6
10	120.4	160.1
15	116.2	163.3
20	111.9	165.7

5°C/min. H_f data were calculated from the melting area under the DSC curve using Universal Analysis 2000 software (TA Instruments).

Mechanical Properties

Tensile strength (TS, MPa; maximum stress on the cross-section of film in the tensile test) and breaking elongation (E, %; percentage of elongation at breakage to the original length of film in the tensile test) were tested using an Instron Universal Testing Machine (5565, Instron, Norwood, MA) at a cross-head speed of 60 mm/min according to GB13022-91. The initial grip separation was set at 50 mm. Prepared samples, each measuring 25 mm wide and 80 mm long, were conditioned at temperature of (23 ± 2)°C and (50 ± 10)% relative humidity for over 4 h before testing. The values were reported as the average of six measurements.

RESULTS AND DISCUSSION

DSC Experimental Results and Analysis

The glass transition temperature (T_g) and the melting temperature (T_m) of SPI/PVA film with different contents of PVA and 1% glycerol obtained from the DSC test are listed in Table I.

Table I shows that each SPI/PVA blend film contains only one value of T_g and T_m. Unique T_g values indicated good compatibility of SPI and PVA, that is, the T_g of the blended films decreased as the PVA content increased, thereby improving the flexibility of the blended films. The strong polyhydroxy hydrogen bonds brought the melting point of PVA close to the decomposition temperature ranging from 220°C to 240°C,[19] which would indicate that PVA was not conducive to thermoplastic processing and heat sealing. The T_m of the blended films increased with increasing PVA content (Table I). Increasing PVA content was indeed disadvantageous to the thermoplastic processability of blended films. However, the blended films exhibited better thermoplastic processability than PVA because the T_m of all SPI/PVA blend films was below 170°C.

Table II lists the heat of fusion (H_f) of SPI/PVA for different components. The blended films had higher melting points when the PVA content increased, which led to an increase in the optimal sealing temperatures of SPI/PVA blended films. Increasing glycerol content reduced the fusion heat of these films because glycerol is a good plasticizer for SPI and PVA, and it has a fluxing action that can be explained by a gel mechanism of plasticization.[19] Plasticization is a dynamic

equilibrium process in which polymer chains dissolve and generate an aggregating force between macromolecules. Several physical cross-linking points arise between the PVA molecules of a certain concentration and temperature, and are subject to change. The plasticizer content in the polymer increases upon collision between solvent molecules. The physical cross-linking change drastically weakens the interaction between polymer chains, macroscopically showing strong plasticizing and fluxing effects. Theoretically, glycerol can reduce the heat-sealing temperature of blended films.

Sealing Parameter Determination

DSC analysis showed that SPI/PVA blended films had T_m values below 170°C, whereas the heat-sealing temperatures were generally higher than T_m for the materials. PVA begins thermal decomposition at ~220°C, that is, the heat-sealing temperature initially lies between 175 and 230°C. Nearly all of the samples had no heat-sealing strength at a sealing temperature of 175°C. Sealing strength occurred only when the temperature reached 180°C. Seal strength identification begins with heat-sealing the samples and manually peeling them off. Seal strength absence is indicated if the samples can easily be peeled off and the failure mode is separation.

An orthogonal experiment was conducted under sealing pressures of 150, 200, 250, 300, and 350 kPa, and dwell times of 0.5, 1.0, 1.5, and 2.0 s, with the sealing temperature at 180°C to verify the existence of seal strength. When the pressure was lower than 350 kPa and the dwell time was less than 2 s, seal strength could not be detected in the samples.

The sealing pressure was 350 kPa, the dwell time was 2 s, and the heat-sealing temperature ranged from 180°C to 230°C.

### Sealing Performance Analysis

Figures 5–7 show the seal strength of SPI/PVA blended film with different glycerol contents. The seal strength increased with PVA content regardless of the glycerol content. When the PVA content was less than or equal to 15%, the seal strength slightly increased with increasing temperature. When the PVA content was 20%, the heat-seal strength increased significantly with temperature, which indicates that the PVA content influenced the heat sealability of the blended film.

With sealing temperatures between 180°C and 220°C (Figure 5), the seal strength of Sample S-20-1 exhibited the fastest growth. The growth rate stagnated at 220°C because of the start of thermal decomposition of PVA, wherein the seal strength was nearly twice that at 180°C. Samples S-20-2 and S-20-3 displayed similar patterns between 180°C and 220°C (Figures 6 and 7). The seal strength growth stagnated at 220°C and 210°C because of the increasing glycerol content.

Table II. The Heat of Fusion of Some SPI/PVA Blend Films

No.	S-5-1	S-10-1	S-15-1	S-20-1
H_f (J g^{-1})	67.78	84.33	94.66	109.93
No.	S-5-2	S-10-2	S-15-2	S-20-2
H_f (J g^{-1})	50.19	67.91	87.11	97.49
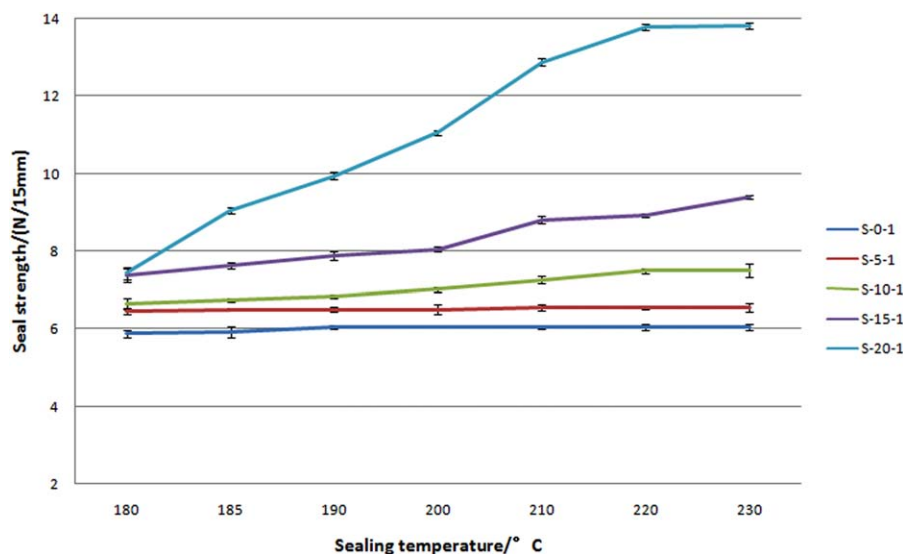
Figure 5. Seal strength of SPI/PVA blended films, each with 1% glycerol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SPI showed good compatibility with PVA, and the PVA component improved the heat-sealing properties of blended film. The seal strength should also continue to increase with continuous increase in PVA content. However, the blended film seal strength development stagnated at ~220°C because of the thermal decomposition of PVA.

For the heat-seal strength tests for the S-x-1 series blend films, 190°C and 220°C (Figure 5) were the breakthrough temperatures for three failure modes (separation, peeling, and breaking). When the sealing temperature was below 190°C, the failure mode was separation; the failure mode was mainly peeling for sealing temperatures between 190°C and 220°C; for temperatures over 220°C, the failure mode was breaking, and blistering was often observed in the sealing area. Blistering is often brought by uneven pressure; this unevenness is not found

in the experiments because of the smoke point of migrated glycerol of over 204°C.[20] At exactly 204°C, glycerol begins to polymerize and decompose to form acrolein.

For S-x-2 and S-x-3 series blended films, the breakthrough temperature of three failure modes were 190°C, 220°C, and 210°C (Figures 6 and 7). When the temperature exceeded 190°C, the macromolecular polymer chains at the blended film interface began to entangle, and more intermolecular forces and hydrogen bonds were produced to provide heat-sealing strength to the blended films.

Increasing the glycerol content leads to an overall decline in seal strength (see Figures 5–7). The seal strength of the film with a 3% glycerol was only half of that with 1% glycerol, for zero PVA content. The heat-seal strength decreased from 13.82 N/15 mm at 220°C (Figures 5) to 10.45 N/15 mm at 220°C (Figures 6), and to
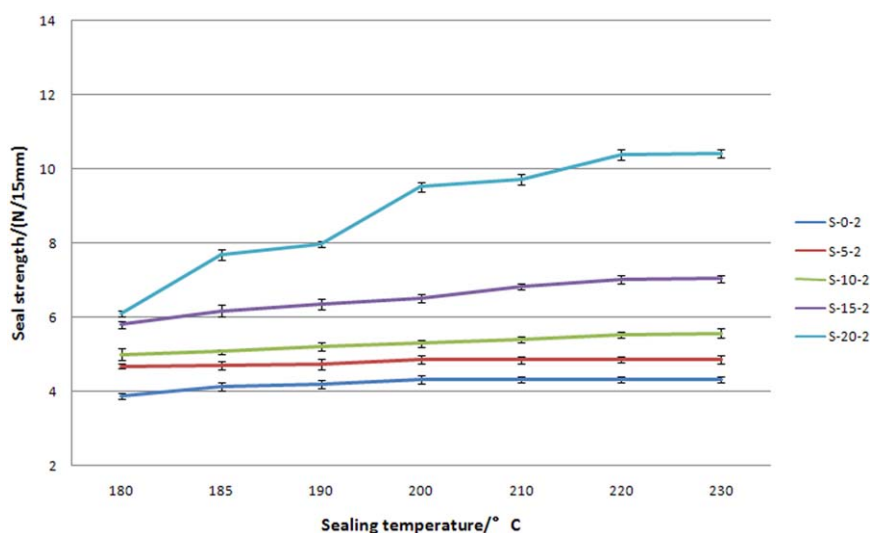
Figure 6. Seal strength of SPI/PVA blended films, each with 2% glycerol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
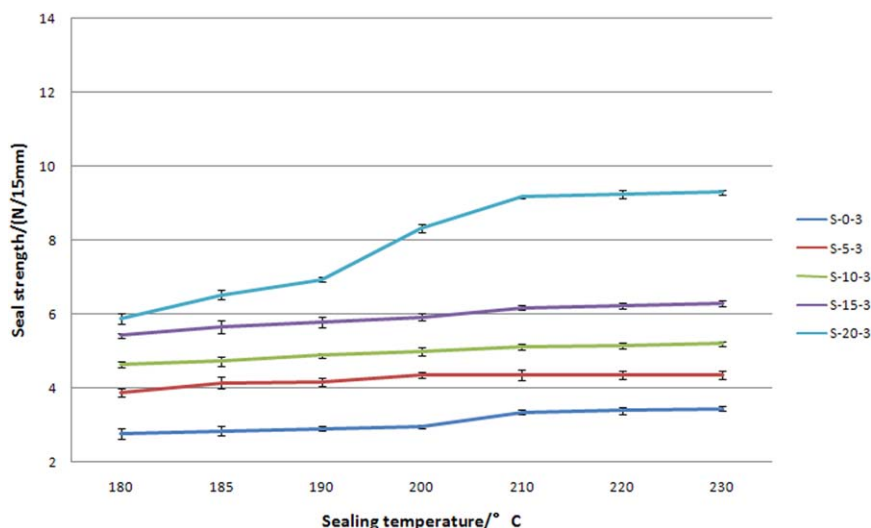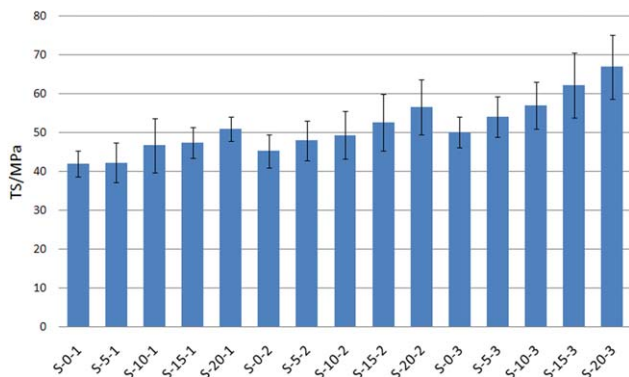
Figure 7. Seal strength of SPI/PVA blended films, each with 3% glycerol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

9.24 N/15 (Figures 7) mm at 210°C, as the glycerol content increased for the case of a 20% PVA blended film. These observations are attributed to the migration of glycerol to the surface, which hindered the entanglement of macromolecular chains at the sealing interface, thereby resulting in decreased seal strength. The enhancement effect of PVA on the seal strength of blended films also weakened with glycerol content increase. The seal strength of blended films was reconciled between the enhancement of PVA and the weakening effect of glycerol.

Figures 8 and 9 describe the mechanical properties of SPI/PVA blended films with different configurations. The tensile strength and breaking elongation increased with PVA content because of the hydrogen bonding and intermolecular forces in polyhydroxy PVA and SPI that made the network structure of SPI more compact, and caused the tensile strength and breaking elongation to increase. The tensile strength of blended films also slightly increased with increasing glycerol content. The increase in breaking elongation was relatively large, which indicated that the desired plasticizing effect of glycerol on the blended film

promoted the interaction between SPI and PVA to a certain extent.

The heat-sealing performance and mechanical properties of the blended films were inconsistent. However, with PVA content retained and glycerol content increased from 1% to 3%, the mechanical strength of the blended film increased, whereas the heat-seal strength decreased. The glycerol migrated to the surface of the blended films and hindered the entanglement of macromolecular chains on the sealing interface although glycerol did plasticize the SPI/PVA system. As a result, the adhesive force at the sealing area was always less than the cohesion force between seal materials. The plasticizing action of glycerol facilitated the entanglement between macromolecules of SPI and PVA to enhance the strength of the blended film; meanwhile, the plasticization hindered diffusion and entanglement of polymer-chain segments at the sealing interface and weakened the seal strength. The temperature increase led to glycerol smoking and blistering of the sealing area, and weakened the film cohesion. The failure mode exhibited breakage at the edge of the sealing area.

Figure 8. The tensile strength TS of SPI/PVA blended films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
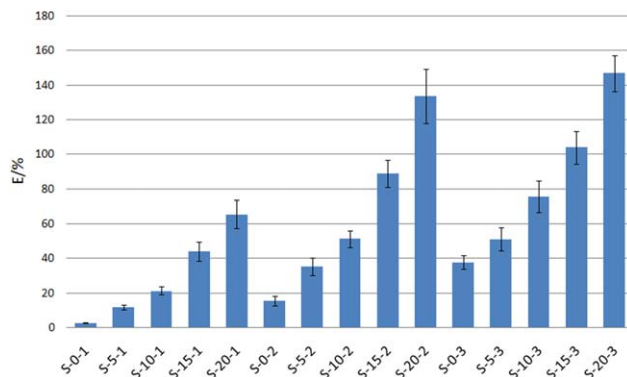
Figure 9. The breaking elongation E of SPI/PVA blended films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Other sealing methods should be considered, such as impulse sealing and ultrasonic sealing. The former is suitable for films that are easily thermally distorted or decomposed, whereas the latter is suitable for the films that are easily thermally distorted but have good sealability by overcoming the contaminants.[21] The interface is heated directly, and the outer surface of the film remains unheated upon application of the two methods. Thus, the cohesive force of the film itself is not reduced and the baseline level of the seal strength can be ensured.

The percentage composition of PVA influences the sealing performance and mechanical properties of the blended film. When the PVA content exceeds 15%, the blended film reaches its maximum seal strength at ∼220°C. Aesthetically unacceptable blistering appears at the seal area when the seal temperature exceeds 200°C. Therefore, the optimal seal temperature is ∼200°C.

CONCLUSIONS

The heat-sealing properties of PVA/SPI films made compatible with glycerol were analyzed. The optimal heat-sealing pressure and dwell time were studied. The influence of sealing temperature, PVA, and glycerol content on the heat-sealing property was determined.

PVA and SPI were compatible at a certain T_g (SPI/PVA blended film had a unique value). The chain entanglement and hydrogen bonding enhanced the mechanical and heat-sealing properties of blended films. PVA dominated the heat-sealing properties of this blended film when the PVA content exceeded 15%, and the maximum seal strength was obtained at 220°C. However, the improvement in heat sealability of blend films was limited because of the narrow window available for the thermoplastic processing of PVA.

Glycerol is a good plasticizer for SPI and PVA. The tensile strength and breaking elongation of the blended film increase with the glycerol content, whereas the heat sealability decreased. These conditions were attributed to the hindrance of entanglement between the macromolecules on the sealing interfaces and the glycerol micromolecules, as well as the vaporization of glycerol at temperatures over 204°C.

The optimal sealing temperature for SPI/PVA blended films should be 200°C (with pressure of 350 kPa and dwell time of 2 s) for usage of conventional heat-sealing methods. Impulse sealing or ultrasonic sealing should be preferred if further improvements to the sealing effect are necessary.

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