Effect of Glycerin on Structure Transition of PVA/SF Blends

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ABSTRACT: Blend films of silk fibrion (SF) and poly(vinyl alcohol) (PVA), with glycerin as an additive, were made, and the structure and properties of the blends were investigated by scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD) and with an Instron Material Tester. The results showed that SF and PVA are principally incompatible and the blends made by the two polymers were phase-separated. The results, however, also demonstrated that the blend structure could be changed to some extent by addition of 3–8% glycerin. The boundary of the PVA and SF phases became indistinct, as reported by SEM, a new peak appeared in the WAXD curves, the width of the OH absorption peak in the FT-IR spectra increased, and the melting points changed in the DSC curves. In particular, the mechanical properties obviously increased, from 350 kg/cm^2 and 10% of PVA/SF (80/20) film to 832 kg/cm^2 and 39% of PVA/SF (80/20) film because of the increase in glycerin. It was suggested that glycerin plays a role in building the relationship between PVA and SF, strengthening the interaction between them and improving their compatibility. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2342–2347, 2002

Key words: silk fibrion; poly(vinyl alcohol); glycerin; structure; property; compatibility

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a nontoxic, water-soluble, biocompatible, and biodegradable synthetic polymer, which can be widely used in biochemical and biomedical materials. PVA has good film-forming properties, highly hydrophilic properties, and high mechanical strength, and has been studied as a membrane in various ways.[1–3] Silk fibroin (SF) fibers from Bombyx mori silkworm are composed of a water insoluble fibrous protein, and recently SF has become one of the most extensively studied materials among the natural biopolymers. It has been exploited as a substrate for enzymes immobilized in the SF membrane,[4,5] as a glucose biosensor by immobilizing glucose oxidase (GOD) within SF membranes, etc.[6,7] However, SF films are very brittle and almost unsuitable for practical use.[8] The inferior tensile properties of SF films can be improved by blending with other natural or synthetic polymers. Recently, Yamaura et al.[9] investigated the syndiotacticity-rich PVA/SF blends and evaluated the degree of swelling in water and their permeability by neutral salts. Tanaka et al.[10] studied properties of SF/PVA blend solutions and phase-separated structure found in the heterogeneous blend films. Tsukada et al.[1] found that PVA and SF are incompatible after analyzing the structure and compatibility of PVA/SF films.

Our interest here is to study structure transition behavior of SF/PVA blends after addition of glycerin to the blends. Because glycerin has the same hydroxyl groups as PVA and SF, there will be some kind of interaction among PVA, glycerin, and SF, causing structure and property changes of SF/PVA blends.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA; DP =1750) purchased from Shanghai Chemical Reagents Company, was dissolved in distilled water by heating in a water bath at 95 °C, and a 5 wt % PVA aqueous solution was prepared. Silk fibroin (SF) fibers from *Bomyx mori* domestic silk were obtained by treating the silk with an aqueous solution of 0.1 wt % Na_2CO_3 at 98 °C for 30 min, and then the fibers were rinsed with warm distilled water and dried at room temperature before use. The fibers were dissolved in mixed solvent $CaCl_2 \cdot CH_3CH_2OH \cdot H_2O$ (mole ratio= 1:2:8) at 78 °C under stirring. The solution was then dialyzed and filtered to obtain liquid silk fibroin with a concentration of ~3 wt%. With addition of glycerin, from Zhenya Chemicals Factory of Suzhou, China, resulting PVA and SF

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TABLE I
Samples and Preparation Conditions for PVA/SF Blend Films

	Sample									
Preparation Condition	1	2	3	4	5	6	7	8	9	10
(a) PVA (wt %)[a]	100	0	80	80	80	80	50	50	50	50
(b) SF (wt %)[a]	0	100	20	20	20	20	50	50	50	50
(c) Glycerin (wt %)[b]	0	0	0	3	5	8	0	3	5	8

[a] The amount of (a) PVA or (b) SF in the films excepting glycerin.
[b] Calculated according to (a) + (b) + (c) = 100 wt %.

solutions were mixed together and slowly and carefully stirred for 2 h at 40 °C. The PVA/SF blend films of 6–7 μm thickness were obtained by casting from the aforementioned solutions onto a polystyrene plate at room temperature, drying in oven for 3 h at 50 °C, and then continually drying at room temperature until a dry film was made. The samples for PVA/SF blends used in this work are shown in Table I.

Characterization

Electrical microscopy was conducted on a DXS-10A scanning electron microscope made by Shanghai Electron and Optics Research Institute, China, at 15kV acceleration voltage after gold coating.

Infrared spectra were measured with an Alpha centauri IR spectrophotometer from Mattson Instruments (Lanham, MA) in the spectral region 4000–400cm^{-1}.

DSC measurements were made with a Perkin-Elmer DSC7 differential scanning calorimeter (PE Inc., Wellesley, MA). The scans were always under a nitrogen atmosphere at a heating rate of 20 °C/min.

Stress–strain behavior was measured with an Instron 1122 Universal Tester (Instron Corporation, Canton, MA) at room temperature. All tests were performed with a specimen width of 10 mm, a gauge length of 60 mm, and a cross head speed of 50 mm/min.

RESULTS AND DISCUSSION

Phase behavior

As observed by Tsukada,[1] the surfaces of pure SF and PVA films were very smooth and there were no traces of particles. However, roundish particles in a homogeneous matrix were observed on the surface of all PVA/SF blends, and the range of particle sizes remained unchanged in spite of the blending ratio. In our experiments, however, after addition of glycerin to SF/PVA blends, there were some changes in the blends. The SEM micrographs of PVA/SF blend films with or without glycerin are shown in Figure 1. As shown in Figure 1(a), the separation phenomena in the blend without glycerin is very distinct, as already mentioned. It is likely that the roundish particles are SF and the homogeneous matrix belongs to PVA. By the addition of glycerin, no obvious phase separation in the micrographs shown in Figures 1(b), (c), and (d) appear, unlike that of the blend in Figure 1(a). Instead, the boundary of the phases is indistinct, and the two phases are close to nearly one system. In addition, the blends with lower SF content (PVA/SF = 80/20) have nearly no particles, as shown in Figures 1(b) and (c), whereas the blends with higher SF content (PVA/SF = 50/50) have obvious particles in Figure 1(d). In fact, the micrographs of Figures 1(b) and (c) have finer particles than that of Figure 1(d). For instance, most of the particles shown in Figure 1(e), which has the same blending constitutes as Figure 1 (c), are small, even if the magnification is larger than that of the other micrographs. The morphological results suggest that phase separation phenomena, occurring in the PVA/SF blends, could be improved by the addition of glycerin to some extent.

Interactions between polymers

The IR spectra of pure PVA, pure SF, and the PVA/SF blend film (80/20) are shown in Figure 2. The pure PVA film [Figure 2(a)] shows absorption bands at 3340, 2942, 1420–1440,1326, 1235, 1095, 916, and 850 cm^{-1} which are attributed to the ν(OH), ν_a(CH$_2$), δ(OH) + ν (CH$_2$), δ(OH) + γ_w(CH), γ_w(CH), ν (C—O), ν_s(C—O), and ν_r(C—H) resonance, respectively, in agreement with the literature data.[11] The pure SF film [Figure 2(c)] shows absorption bands at 1652 cm^{-1} (amide I), 1540 cm^{-1} (amide II), and 1232 and 650 cm^{-1}(amide V), attributed to SF with random coil conformation.[12] In addition, the band at 650 cm^{-1} is assigned to the silk I crystals.[13] The spectrum of the PVA/SF (80/20) blend film [Figure 2(b)] is characterized by the presence of absorption bands typical of the pure components, whose intensity is roughly between that of pure PVA and pure SF films. However, as shown in Figure 3, for PVA/SF blends (PVA/SF), with the addition of glycerin, changes can be observed in the —OH stretching region (3500–3200 cm^{-1}); that is, the width of the —OH absorption peaks increase with increasing the content of glycerin in PVA/SF films, which could characterize the increase of the intensity

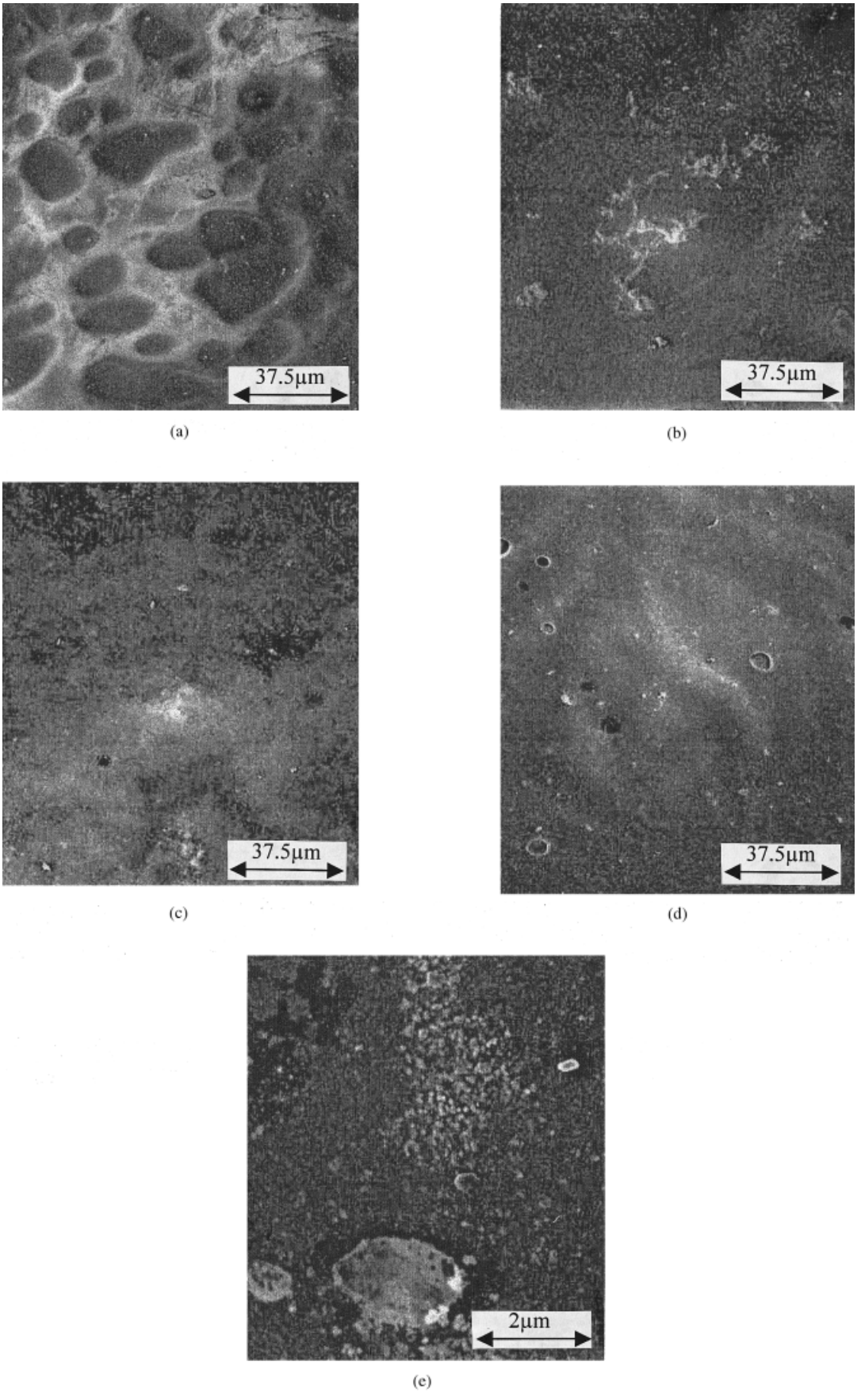

Figure 1 SEM micrographs of PVA/SF bend films: (a) PVA/SF (80/20) blend; (b) PVA/SF (80/20)/glycerin (5%); (c) PVA/SF (80/20)/glycerin (3%); (d) PVA/SF (50/50)/glycerin (5%); (e) PVA/SF (80/20)/glycerin (3%).

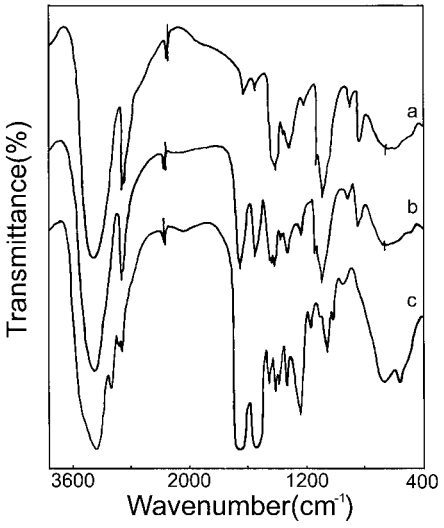

Figure 2 IR scans of PVA/SF blend films: (a) PVA; (b) PVA/SF (80/20); (c) SF.

of hydrogen bond.[14] The modification of the frequencies leads us to think that the presence of glycerin induces the occurrence of intermolecular interactions between the two polymers, mainly due to hydrogen bonding as hydroxyl groups of PVA—hydroxyl groups of glycerin —amide groups of SF. The polar hydroxyl groups of glycerin act with molecular chains of SF, preventing hydrogen combination between SF molecular chains.[15] Similarly, the hydroxyl groups can act with PVA molecules. Therefore, glycerin plays a role of building relationship between PVA and SF and strengthens the interaction between them.

The IR spectra of PVA/SF blend films of the blending ratio 50/50, with or without glycerin, are shown in Figures 4(a) and (b), respectively. Compared with the spectrum without glycerin, as shown in Figure 4(b),

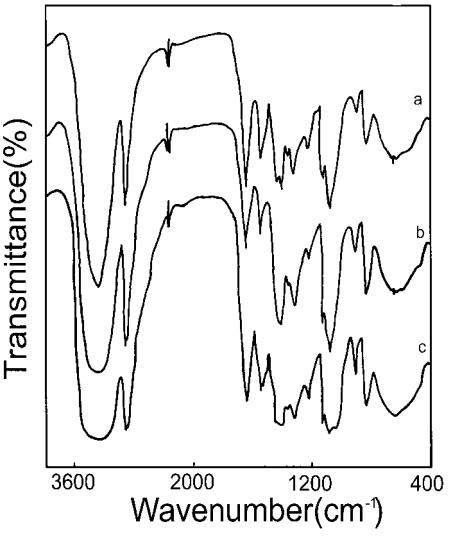

Figure 3 IR scans of PVA/SF blend films (PVA/SF = 80/20). Content of glycerin: (a) 3%; (b) 5%; (c) 8%.

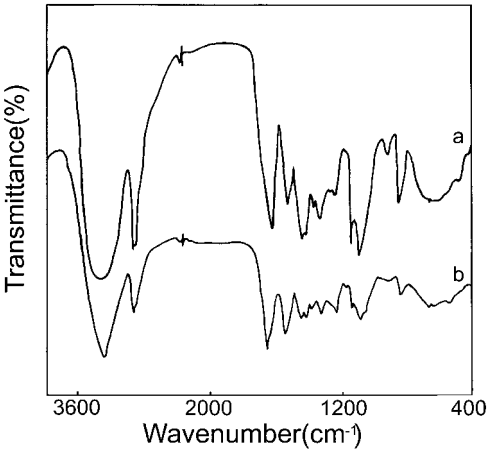

Figure 4 IR scans of PVA/SF blend films (PVA/SF = 50/50). Content of glycerin: (a) 5%; (b) 0.

the addition of glycerin causes the width of —OH absorption peak at ~3250 cm^{-1} increase, as shown in Figure 4(a). This result indicates when the ratio PVA/SF of the blend increases from 80/20 to 50/50, glycerin is also in favor of increasing interactions between PVA and SF.

X-ray diffraction

X-ray diffraction curves of the pure PVA, the pure SF, and PVA/SF films are shown in Figure 5. Pure PVA film [Figure 5(b)] shows a less intense peak at $2\theta = 11.9°$, in addition to a major diffraction peak at $2\theta = 20.5°$. The X-ray diffraction curve of SF film [Figure 5(d)] exhibits a major and broad 2θ peak at 20.6° and a minor peak at 9.7°, that is assigned to the silk I crystalline structure.[12] The diffraction curve of the

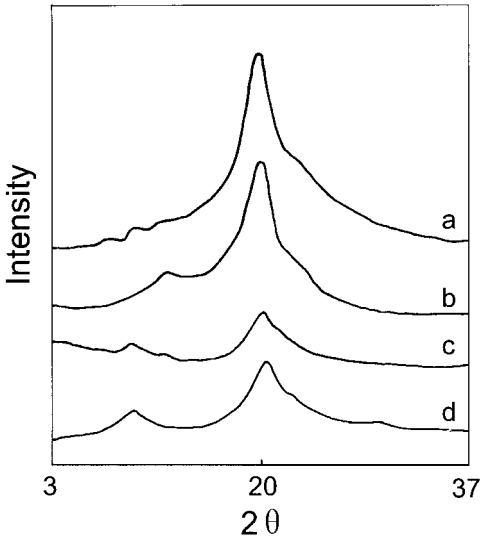

Figure 5 WAXD curves of PVA/SF blend films:(a) PVA/SF (80/20)/glycerin (5%); (b) PVA; (c) PVA/SF (80/20); (d) SF.

PVA/SF (80/20) blend film [Figure 5(c)] without glycerin shows major peaks in the vicinity of 20.5, 11.9, and 9.7°, corresponding to the peaks in the diffraction curves of pure PVA and pure SF. Thus, it is evident that microcrystals of the PVA and SF films exist separately, showing microphase separation between PVA and SF, which is agree with Lu's report.[15] The addition of glycerin to PVA/SF blend film [Figure 5(a)] causes a new peak at about 7.4°, which suggests that a new structure has been formed between PVA and SF that is related to the increase of interactions between PVA and SF.

Thermal properties

The DSC curves of pure SF, pure PVA, and PVA/SF (80/20) blend films are shown in Figure 6. The pure PVA film displays a major endothermic peak at ~228 °C, which has been attributed to the melting of PVA, whereas the pure SF film displays a major endothermic peak at ~285 °C, which is caused by the thermal decomposition. As concerns the blend, with the increase of glycerin, the melting peak shifts towards the low temperature. When the concentration of glycerin is zero, the peak is at 227.5 °C, approaching the position of the peak for pure PVA film. When the concentration of glycerin is 3%, the peak is at 225 °C. When the concentration is 5%, the peak temperature lowers to ~215 °C. On the other hand, the peak at 285 °C of pure SF still appears in the blend. It, however, is kept at the same temperature in spite of addition of glycerin to the blend.

Mechanical properties

Stress–strain curves of the pure SF and PVA/SF blend films are shown in Figure 7. The pure SF film has very low strength of ~158 kg/cm^2, showing that silk film in the dry state is generally unsuitable for practical uses because of its high degree of brittleness. The addition of PVA to SF is effective in inducing significant changes in the mechanical properties of the resulting blend films. Although strength and elongation of the blend films are above that of the pure silk film, the value is relatively low compared with the blends with the addition of glycerin. The strength and elongation at break of the PVA/SF blend film are 350 kg/cm^2 and 10%, respectively. As indicated by Tsukada[1] and already described, SF and PVA constituents can form two separate phases and the blends are incompatible, so the increase of mechanical properties is limited.

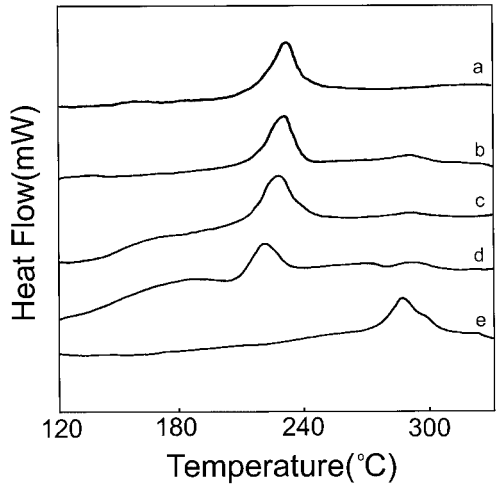

Figure 6 DSC curves of PVA/SF blend films: (a) PVA; (b) PVA/SF (80/20); (c) PVA/SF (80/20)/glycerin (3%); (d) PVA/SF (80/20)/glycerin (5%); (e) SF.

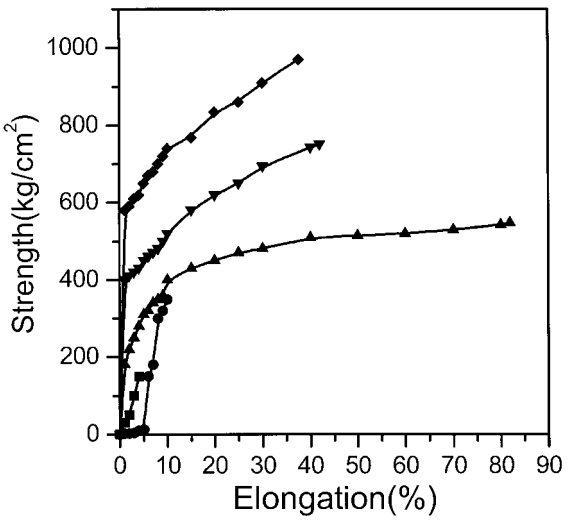

Figure 7 Stress–strain curves of PVA/SF blend films.Key: (♦) PVA/SF (80/20)/glycerin (3%); (▼) PVA/SF (80/20)/glycerin (5%); (▲) PVA/SF (80/20)/glycerin (8%); (●) PVA/SF (80/20); (■) SF.

The addition of glycerin to the blends seems to play a role in increasing strength and elongation of the blend. As shown in Figure 7, the behavior of strength and elongation varies according to the glycerin content. If glycerin content is 3%, although the strength can reach 832 kg/cm^2, the elongation at break is only 39%. If, however, glycerin content increases to 5%, the strength decreases to 426 kg/cm^2, while elongation increases to 53%. It is likely that the decrease of the strength indicates that the effect of plastification of glycerin on decrease of strength exceeds the effect of compatibilization on the increase of strength. The reason for the increase of elongation is the addition of glycerin, the hydroxyl groups of which interact with the PVA and SF molecular chain, leading to larger gaps among PVA molecules and SF molecules. The molecular chain movement becomes easy, so the softness and elasticity of the films increase. When the ratio of PVA/SF of the blend film increases from 80/20 to 50/50, phenomena similar to those already described appear, as shown in Figure 8.

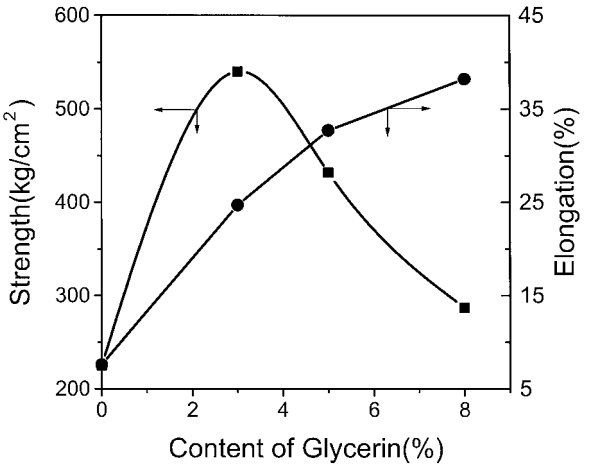

Figure 8 Relation between mechanical properties and the content of glycerin in PVA/SF (50/50) blends.

CONCLUSIONS

According to SEM, the separation phenomenon of the PVA/SF blend is distinct, while the boundary of the phases of the PVA/SF blend film with glycerin is indistinct, which suggests that phase separation in the PVA/SF blends could be improved by the addition of glycerin. IR, WAXD, DSC, and mechanical property measurement demonstrate structural change of PVA/SF blend films with the addition of glycerin. The presence of glycerin induces the occurrence of intermolecular interactions between the two polymers mainly due to hydrogen bonding of hydroxyl groups of PVA—hydroxyl groups of glycerin—amide groups of SF.

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