

Morphology and Mechanical Properties of Pullulan/Poly(vinyl alcohol) Blends Crosslinked with Glyoxal

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ABSTRACT: We prepared pullulan/poly(vinyl alcohol) (PVA) blend films by casting the polymer solution in dimethyl sulfoxide. Their morphology and mechanical properties were investigated. Scanning electron micrographs revealed that the pullulan was immiscible with PVA over the entire composition range. The tensile strength and modulus of the blend films were lower than those predicted by the upper bound composite equation. To improve the mechanical properties, we investigated the reaction of the 40/60 blend with glyoxal. The infrared spectral change and the increase in the glass-transition temperature (corresponding to the PVA component) accompanying the reaction indicated that crosslinking with glyoxal had proceeded. The crosslinked films were homogeneous and had higher tensile strengths and moduli than the simple blend. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2273–2280, 2001

Key words: crosslinking; blends; pullulan; poly(vinyl alcohol); biodegradable polymer

INTRODUCTION

Pullulan is a linear polymer possessing maltotriose units connected by (1-6)- α -D linkages (Fig. 1), and it is known as a biodegradable polymer. The polymer is prepared by the culturing of *Aureobasidium pullulans* with starch or sugar. Pullulan is a water-soluble polysaccharide with low oxygen permeability, and it is used for food coating and drug processing. Although recently several chemical modifications of pullulan have been investigated for imparting thermoplastic properties and water resistance,^{1–3} little has been re-

ported in the literature about blends of pullulan and biodegradable, synthetic polymers.

Poly(vinyl alcohol) (PVA) is a well-known biodegradable polymer with a high tensile strength and adhesive property. PVA with a high degree of saponification (DS) is water-resistant at room temperature. Blends of PVA with polysaccharides such as starch and cellulose have been reported by several groups. Nishio and Manley⁴ found that cellulose/PVA blends exhibited considerable miscibility above a 60 wt % cellulose content in contrast to the immiscibility of starch/PVA blends. Otey et al.⁵ applied a starch/PVA blend coated with Saran or poly(vinyl chloride) to biodegradable agricultural mulch. Westhof et al.⁶ described how the percentage elongation of a starch/PVA film was improved by the addition of polyol plasticizers such as glycol glycoside. Chen et al.⁷ observed an improvement in the mechanical properties of starch/PVA films by crosslinking with

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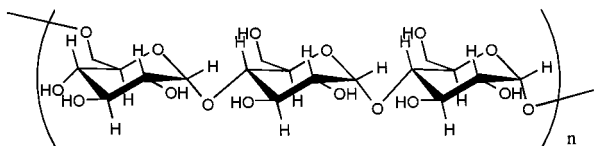


Figure 1 Structure of pullulan produced from *Aureobasidium pullulans*.

hexamethoxymethylmelamine. According to Miya and coworkers,^{8,9} chitosan forms a clear homogeneous blend with PVA, and a synergistic effect on the tensile strength of the blend can be observed. Miyashita et al.¹⁰ reported that partially deacetylated chitin was miscible with PVA. Kim et al.¹¹ found that the tensile strength of chitosan/PVA blend films crosslinked with glutaraldehyde increased with an increasing amount of the crosslinking reagent.

This article describes the morphology, mechanical properties, and water resistance of pullulan/

PVA blends. In particular, the effect of the crosslinking of the blend with glyoxal was investigated.

MATERIALS AND METHODS

Materials

Pullulan, PF-20-grade [number-average molecular weight (M_n) = 200,000–250,000], was supplied by Hayashibara Biochemical Laboratories, Inc. (Okayama, Japan). Two grades of PVA were obtained from Kuraray Co., Ltd. (Tokyo, Japan): PVA-124H, 99% DS (M_n = 107,000), and PVA-420, 80% DS (M_n = 105,000). Dimethyl sulfoxide (DMSO) was purchased from Kishida Chemical Co., Ltd. (Osaka, Japan), 40% glyoxal aqueous solution was acquired from Wako Pure Chemicals Industries, Ltd. (Osaka, Japan), and other re-

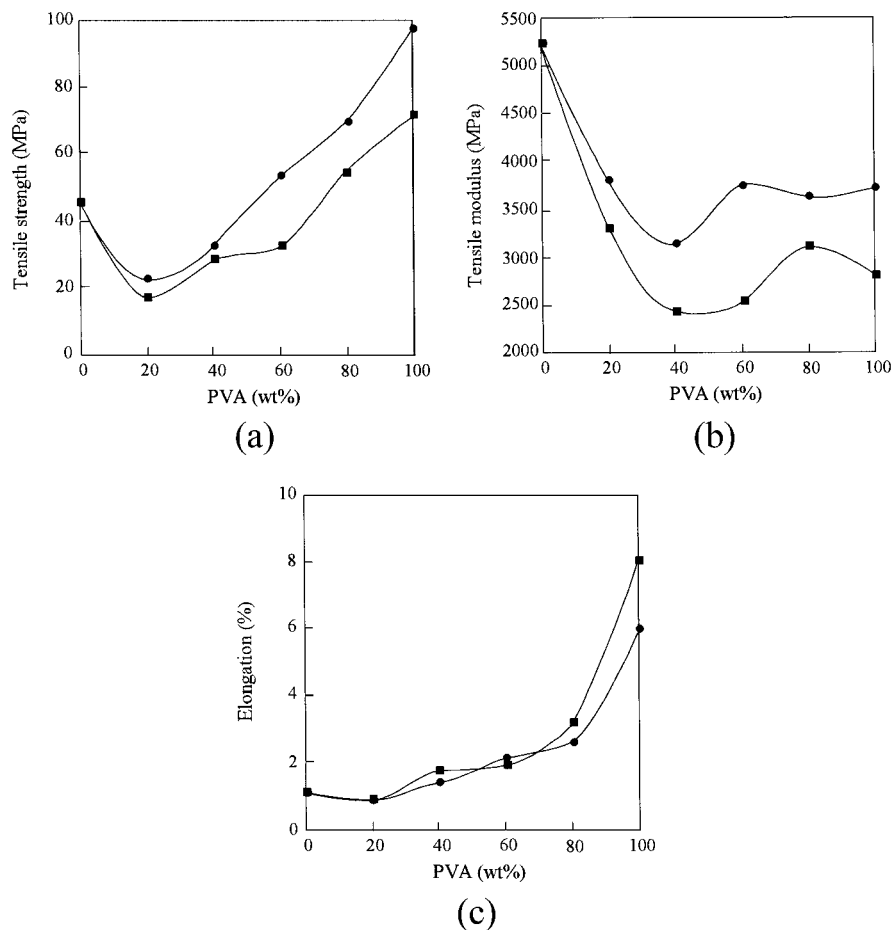


Figure 2 Tensile properties of pullulan/PVA blend films. (a) The tensile strength, (b) tensile modulus, and (c) elongation at break are plotted as functions of the PVA content: (●) 99 and (■) 80% DS.

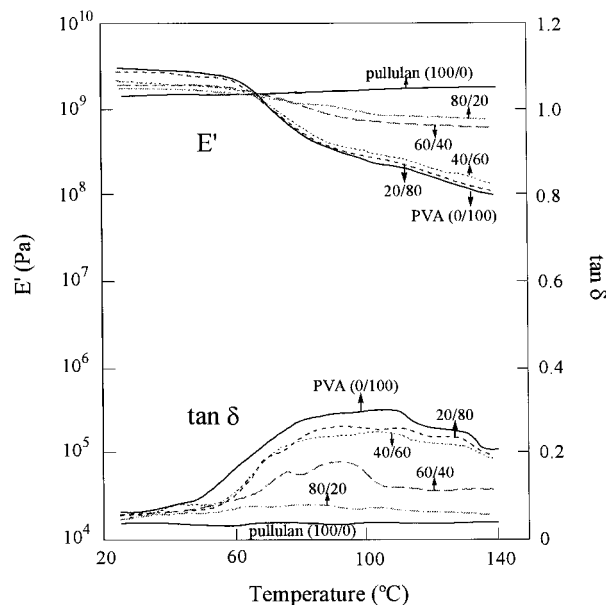


Figure 3 Dynamic viscoelastic curves of pullulan/PVA blend films (99% DS PVA). The storage modulus (E') and $\tan \delta$ are plotted as functions of temperature.

agents were from Kanto Chemicals Co., Inc. (Tokyo, Japan).

Preparation of Pullulan/PVA Blend Films

Pullulan/PVA blend films were prepared as follows. Pullulan and PVA (99 or 80% DS) were mixed in DMSO at various ratios [pullulan/PVA = 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100 (wt %)]. A mixture containing 6 wt % polymer in all was stirred at 80°C to be dissolved. This solution was cast on a polyethylene plate and dried at 60°C for 24 h. The dried blend film was washed with methanol and dried again at 60°C for 24 h under vacuum.

Measurement of the Properties of Blend Films

The tensile strength and modulus were measured at room temperature on an AGS-500C automatic tensile test machine (Shimadzu Co., Kyoto, Japan) at a tensile speed of 10 mm/min. Dynamic viscoelastic measurements were performed on a Rheograph Solid (Toyo Seiki Co., Ltd., Tokyo, Japan) at a frequency of 10 Hz and a heating rate of 2°C/min.

We assayed water resistance by measuring the weight loss of the sample after immersion in water at 25°C for 24 h and drying for 24 h under vacuum. The blend film was coated with gold, and the morphology was observed via scanning elec-

tron microscopy (SEM) with a JSM-6300 (Japan Electron Co., Ltd., Tokyo, Japan).

Crosslinking Reaction

p-Toluene sulfonic acid (0.1 wt %) was added as an acid catalyst to the 6 wt % polymer solution (pullulan/PVA = 40/60) in DMSO. A glyoxal aqueous solution (40%) was added to the mixture and stirred at 60°C for the prescribed time. The molar ratio of the total aldehyde groups to the total hydroxyl groups of pullulan (CHO/OH) was 1.0. The reaction solution was cast on a polyethylene plate and dried at 60°C for 24 h. The dried film of the blend was washed with methanol and dried at 60°C for 48 h under vacuum.

Infrared (IR) spectra of the crosslinked blend films were measured on an FTIR-8100 (Shimadzu Co.).

RESULTS AND DISCUSSION

Mechanical Properties of Pullulan/PVA Blend Films

The tensile properties of pullulan/PVA blend films with various PVA contents were tested. The strength and modulus showed the lowest values at PVA contents of 20 and 40 wt %, respectively [Fig. 2(a,b)]. The tensile strength and modulus of the blend films were lower than those predicted

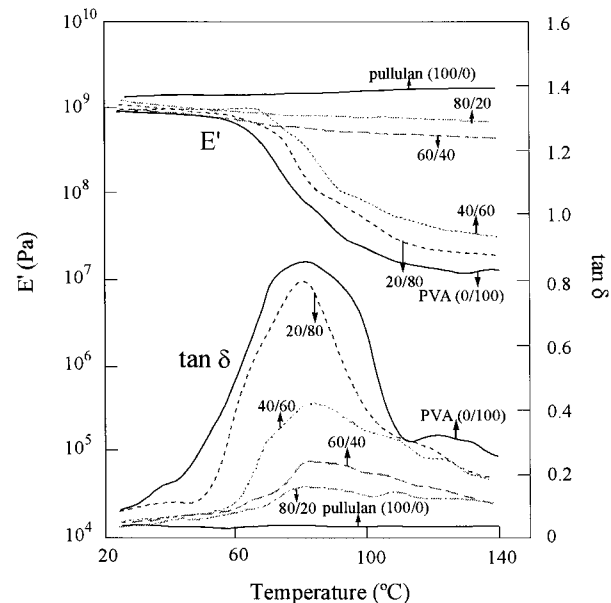


Figure 4 Dynamic viscoelastic curves of pullulan/PVA blend films (80% DS PVA). The storage modulus (E') and $\tan \delta$ are plotted as functions of temperature.

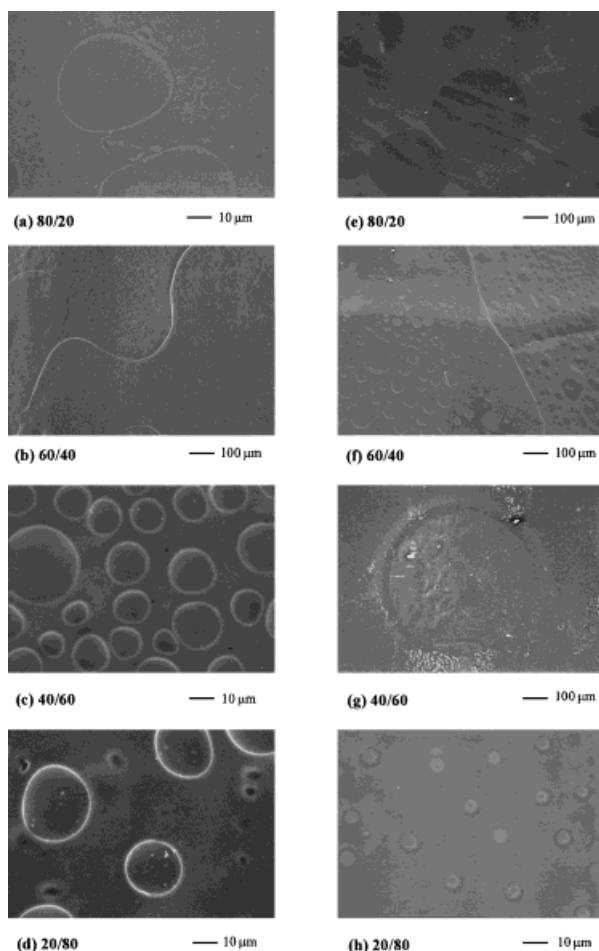


Figure 5 SEM micrographs of blend films of pullulan and PVA with (a–d) 99 and (e–h) 80% DS. Pullulan/PVA composition ratios were (a,e) 80/20, (b,f) 60/40, (c,g) 40/60, and (d,h) 20/80.

by the upper bound composite equation over the entire composition range, indicating that this blend was phase-separated and that the interfacial adhesion between PVA and pullulan was poor. This tendency was more significant for the blend containing PVA with an 80% DS. The elongation at break of the blend films was much lower than that of the pure PVA film [Fig. 2(c)].

Figures 3 and 4 show the storage modulus and $\tan \delta$ versus temperature, as evaluated by dynamic viscoelastic measurements, for a pullulan/PVA blend (99% DS) and a pullulan/PVA blend (80% DS), respectively. The storage modulus of pure pullulan was almost constant in from 20 to 140°C. However, the storage modulus of the blend films with PVA contents of 60 and 80% and pure PVA dropped around 60–100°C. The drop in the modulus was not so pronounced for the blend with PVA contents of 20 and 40%, indicating that PVA

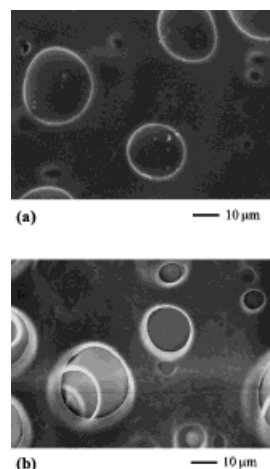


Figure 6 SEM micrographs of blend films composed of 20% pullulan and 80% PVA (a) before and (b) after immersion in water for 24 h (99% PVA DS).

particles were dispersed in the pullulan matrix for the pullulan-rich blend. Broad $\tan \delta$ peaks that were related to the glass transition of the amorphous PVA region^{4,12} appeared around 60–140 and 40–110°C for pure PVA films with 99 and 80% DSs, respectively. The 80% DS PVA showed

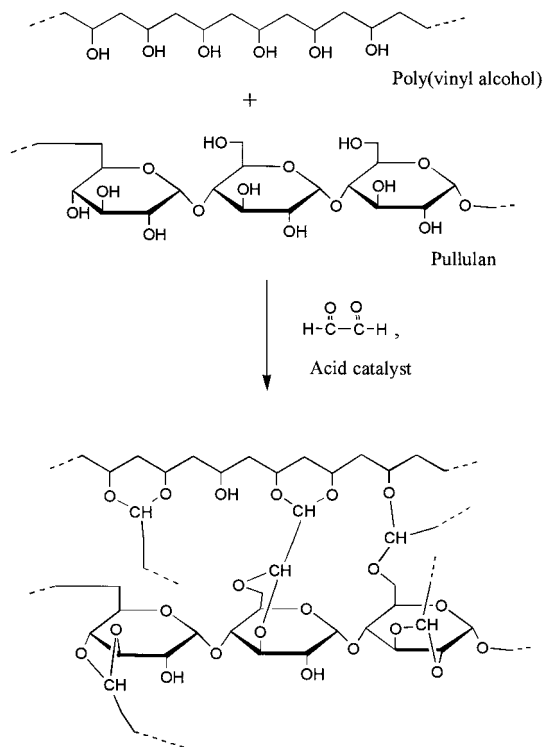


Figure 7 Schematic representation of the reaction of aldehyde (glyoxal) with hydroxyl groups of pullulan and PVA.

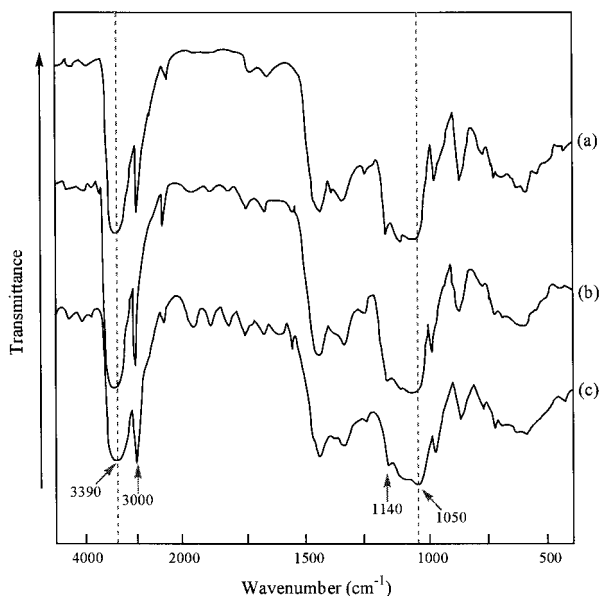


Figure 8 IR spectra of crosslinked pullulan/PVA (40/60) blend films: (a) a blend film without crosslinker and (b,c) a blend film prepared in a reaction with glyoxal for 2 and 3 h, respectively.

a higher $\tan \delta$ peak height and a larger drop of modulus than the 99% DS PVA, indicating that the degree of crystallinity of 80% DS PVA was lower than that of 99% DS PVA. Also, 80% DS PVA showed a slightly lower $\tan \delta$ peak temperature than 99% DS PVA, indicating that the hydrogen-bond interaction of 80% DS PVA was weaker than that of 99% DS PVA because of the difference in the hydroxyl group content. The effect of PVA content on the $\tan \delta$ peak temperature was not significant. This result suggests that pullulan is immiscible with PVA.

Morphology of Pullulan/PVA Blends

Figure 5 shows SEM micrographs of pullulan/PVA blends. The blends showed a macro phase-separated morphology over the entire composition range. On the basis of the composition of the blends, it appeared that the minor component of the blend was dispersed in the matrix of the rich component. The average particle size of the dispersed phase varied with the blend composition. The poor dispersion observed in the pullulan/PVA (60/40) blend is in agreement with its poor tensile properties.

Figure 6 shows SEM micrographs of the pullulan/PVA (99% DS) 20/80 blend film after immersion in water for 24 h. As expected because PVA with a higher DS was hardly soluble in water and

pullulan was soluble at room temperature, the pullulan particles dispersed in the PVA matrix were removed to afford a 10–20- μm porous structure.

Characterization of Crosslinked Pullulan/PVA Blends

Pullulan and PVA were crosslinked with aldehyde for the improvement of the miscibility of pullulan and PVA. Aldehyde reacts with hydroxyl groups in the presence of an acid catalyst to give hemiacetal or acetal (Fig. 7). Two-functional glyoxal was used for the crosslinking of pullulan and PVA. PVA with a 99% DS was used for the preparation of crosslinked blend films, and the composition of the blends was fixed at 40/60 pullulan/PVA.

An IR spectrum of the crosslinked blend film was compared with that of a blend film without crosslinker (Fig. 8). The absorption band corresponding to hydroxyl groups of pullulan and PVA (3390 cm^{-1}) was reduced relative to the band of CH stretching vibrations (3000 cm^{-1}) as the crosslinking reaction proceeded. The increase in absorption corresponding to ether bonds of acetal groups (1050 cm^{-1}) indicated that hydroxyl

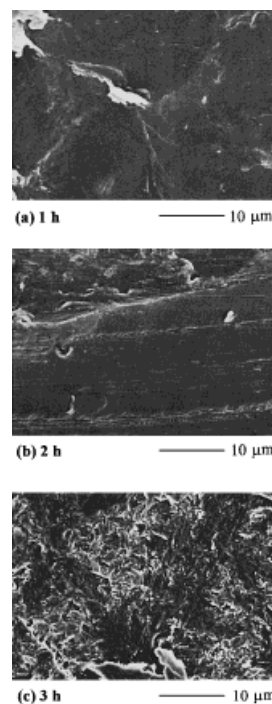


Figure 9 SEM micrographs of pullulan/PVA (40/60) blend films crosslinked with glyoxal. Polymer blends were subjected to crosslinking reactions for (a) 1, (b) 2, and (c) 3 h, respectively.

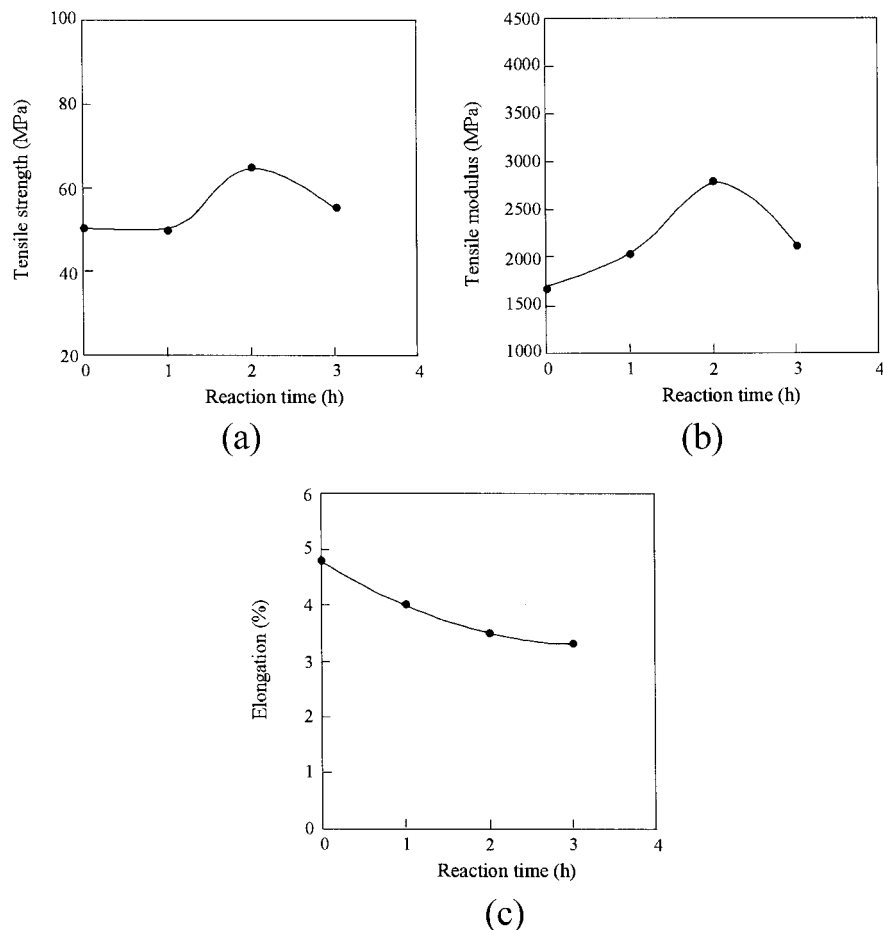


Figure 10 Tensile properties of pullulan/PVA (40/60) blend films crosslinked with glyoxal. (a) The tensile strength, (b) tensile modulus, and (c) elongation at break are plotted as functions of the crosslinking reaction time.

groups of pullulan and PVA reacted with glyoxal to give acetal groups. The absorption corresponding to the crystallization-sensitive band of PVA at 1140 cm^{-1} decreased in the crosslinking reaction. Our thoughts about this result are described later.

Morphology of Crosslinked Pullulan/PVA Blends

Figure 9 shows electron micrographs of the blend films crosslinked with glyoxal. The crosslinked blend films were miscible. This result suggested that crosslinking with glyoxal strengthened the interaction between pullulan and PVA molecules. Homogeneity was observed in the films prepared at reaction times over 1 h, and numerous microcracks were contained in the films prepared at a reaction time over 3 h. The reaction solution containing glyoxal began to gelate 3 h after the reaction was started. It is thought that these cracks might have occurred during the process of the

crosslinked films drying because the gelation of the blend was not uniform.

Water resistance was improved by the crosslinking. For the blend films reacted with glyoxal for 3 h, the weight loss after immersion in water for 24 h was 30%, whereas the weight loss was 40% for films without crosslinking.

Mechanical Properties of Pullulan/PVA Crosslinked Blend Films

The tensile properties of the blend films were varied with the crosslinking reaction time. For blend films crosslinked with glyoxal, the tensile strength and tensile modulus showed the highest values at the reaction time of 2 h, although the elongation at break gradually decreased with the reaction time (Fig. 10). The tensile properties of the blends decreased at the reaction time of 3 h. The lowering of the tensile properties of the crosslinked film prepared by the 3-h reaction should be attributed to the

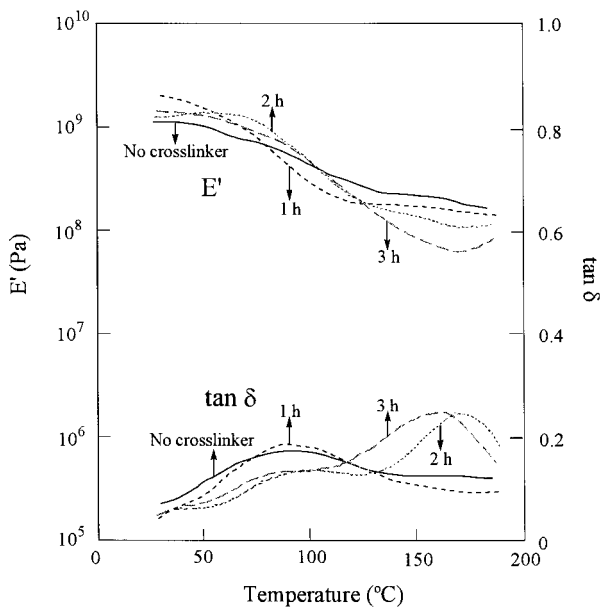


Figure 11 Dynamic viscoelastic curves of pullulan/PVA (40/60) blend films crosslinked with glyoxal. The storage modulus (E') and $\tan \delta$ are plotted as functions of temperature with different reaction times.

formation of microcracks described in the previous section. These results are thought to be caused by intermolecular crosslinking.

Figure 11 shows dynamic viscoelastic curves of blend films crosslinked with glyoxal as a function of temperature. The storage modulus below 60°C for the crosslinked blends was higher than that of the blend without crosslinker. The $\tan \delta$ peak around 70–110°C, related to the relaxation of the amorphous region of PVA, became weak, and a new $\tan \delta$ peak appeared temperatures greater than 150°C. These results suggest that the glass-transition temperature related to the PVA component arose with the crosslinking of the PVA component. However, the storage modulus for the crosslinked blend films remarkably decreased at the elevated temperature, compared with the blend film without crosslinking. The decrease may be due to the loss of the crystalline region. The decrease in the storage modulus around the 60–120°C became steeper as the crosslinking reaction proceeded. This indicates that the amorphous region of the crosslinked blend increased with the reaction time. The polymer network may be weakened at a high temperature. The storage modulus of the blend crosslinked for 3 h was the lowest at a high temperature, probably because of the microcracks observed with SEM. In a comparison of IR spectra of the crosslinked blend film and the blend film without crosslinking, the ab-

sorption corresponding to the crystallization-sensitive band of PVA at 1140 cm^{-1} decreased in the crosslinking reaction (Fig. 8). This observation indicates a loss of the crystalline region in the crosslinked blend film, and this is consistent with the large decrease in the storage modulus for the crosslinked blend film around 60–120°C with respect to the blend without crosslinker.

The peak shift of the $\tan \delta$ plot was not observed in the 1-h reaction, whereas the morphology of the blend was homogeneous. In an IR spectrum of a blend film reacted with glyoxal for 3 h, the absorption peak of the hydroxyl groups (3390 cm^{-1}) still remained to a considerable extent [Fig. 8(c)]. Also, the $\tan \delta$ peak corresponding to PVA remained in the dynamic mechanical spectrum of the blend film (Fig. 11). These results indicate that the reaction of glyoxal with hydroxyl groups of pullulan and PVA was not completed in 3 h. This is in agreement with the insufficient water resistance of the crosslinked product. The formation of a homogeneous morphology by crosslinking may be caused by the action of the pullulan/PVA block copolymer generated by the partial reaction with glyoxal as a compatibilizer.

CONCLUSIONS

The effects of crosslinking pullulan/PVA blends with glyoxal on the morphology, mechanical properties, and water resistance were investigated.

A comparison of the IR spectra and dynamic viscoelastic curves between the pullulan/PVA blends with and without glyoxal revealed that the partial crosslinking of pullulan and/or PVA proceeded with the formation of acetal groups. The mechanical properties and water resistance were improved by crosslinking. With respect to the morphology of the blends, we found that the blend film crosslinked with glyoxal was homogeneous, whereas pullulan and PVA were immiscible. We demonstrated that the crosslinking of pullulan/PVA blends with glyoxal is an effective method for improving the physical properties of the film.

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