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ORIGINAL CONTRIBUTION

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Morphology and mechanical properties of poly(vinyl alcohol) and starch blends prepared by gelation/crystallization from solutions

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Abstract In an attempt to produce biodegradation materials, poly(vinyl alcohol) (PVA)–starch (ST) blends were prepared by gelation/crystallization from semidilute solutions in dimethyl sulfoxide (Me_2SO) and water mixtures and elongated up to 8 times. The content of mixed solvent represented as Me_2SO/H_2O (volume percent) was set to be 60/40 assuring the greatest drawability of PVA homopolymer films. The PVA/ST compositions chosen were 1/1, 1/3, and 1/5. The elongation up to 8 times could be done for the 1/1 blend but any elongation was impossible for blends whose ST content was beyond 50%. When the blends were immersed in water at 20 or 83 °C, the solubility became considerable for an undrawn blend with 1/5 composition and a drawn 1/1 blend with $\lambda = 8$. To avoid this phenomenon, cross-linking of PVA chains was carried out by formalization under formaldehyde vapor. Significant improvement could be established by the cross-linking of PVA chains. For the 1/1 blend, the amount of ST dissolved in water at 23 °C was less than 3% for the undrawn state and 25% for the drawn film. The decrease in the ST content was enough for use as biodegradation materials. Namely, the water content relating to the biodegradation in soil is obviously different from such a serious experimental condition that a piece of blend film was immersed in a water bath. At temperatures above 0 °C, the storage modulus of the formalization blends became slightly higher than those of the nonformalization blends. The Young's modulus of the drawn films with a draw ratio of 8 times was 2 GPa at 20 °C.

Key words Poly(vinyl alcohol)–starch blends · Gelation/crystallization · Dimethyl sulfoxide and water mixtures · Formaldehyde · Cross-linking

Introduction

It is of interest to produce high-modulus and high-strength materials with biodegradation. Recent studies of polyethylene (PE) have reported a slight degree of biodegradation, although PE ranks among the stable polymers [1–10]. Studies of the degradation have been mainly done for low-density PE (LDPE) and high-density PE (HDPE) by Albertsson and coworkers [1– 8]. They pointed out that biodegradation of PE is affected by preliminary irradiation with a UV source, by antioxidant [4], by additives [5, 6], and by molecular weight [2]. Initial photooxidant facilitates an attack of PE by microorganisms owing to a synergistic effect between photooxidant and biodegradation [6–8]. According to recent reports by Ootaki and coworkers [9, 10], the biodegradation of PE becomes significant by the introduction of starch (ST). This is due to the enticement of microscopic organisms, although starch particles were not directly concerned with the degradation of PE. Unfortunately, Young's modulus and the tensile strength of the LDPE and HDPE reported in some articles were too low to use them as commercial films and fibers, despite a starch content of less than 10% [11].

As for further investigation, Nakashima and Matsuo [11] investigated development of high-strength and high-modulus PE–ST composite films and biodegradation of the composite films. The PE–ST compositions chosen were 3/1, 1/1, 1/3, and 1/5. The maximum draw ratio of the 1/5 composite reached 80 and the corresponding Young's modulus was 10 GPa. The values for the films with the 3/1 and 1/1 composites were about 105 and 75 GPa, respectively, higher than the moduli of aluminum (70 GPa) and cast iron (90 GPa). In spite of the elongation up to 80 times, most of the ST particles remained within the composite films. The films with different compositions were put on a decarbonized agarose bench containing mineral nutrients, which had been prepared as an isolate filamentous fungi medium in a Petri dish. However, the degradation of PE was not so significant. Accordingly, poly(vinyl alcohol) (PVA) was used instead of PE, since PVA is well known as a biodegradation polymer and the drawn fiber (or film) provides a high modulus and high strength.

Ultradrawing of PVA has been carried out as one of concepts to produce high-strength and high-modulus materials [12–15]. Cha et al. [12] succeeded in producing high-modulus PVA fibers by drawing gels prepared by crystallization from semidilute solutions in dimethyl sulfoxide (Me_2SO) and water mixtures. According to their work, the maximum drawability was assured when a solution with 70/30 composition was quenched at temperatures below −50 °C. The resultant tensile strength and Young's modulus of the drawn fiber reached 2.8 and 60 GPa, respectively. In this work, the composite materials of PVA and ST were prepared by gelation/crystallization of the mixed solutions to obtain biodegradation materials with high modulus and high strength. In our case, the maximum Young's modulus was confirmed by preparing specimens with solutions of 60/40 composition [15]. To avoid ST domains accidentally flowing out of the PVA medium, cross-linking of PVA chains within the blends was carried out by formalization.

Experimental

The samples used in this experiment were PVA powder with a polymerization of 2000 and 98% hydrolysis and corn ST treated with a silane coupling agent. The PVA gels with ST were prepared by crystallization from semidilute solutions in Me_2SO and water mixtures, the concentration of PVA against the mixed solvent being 10 g/100 ml. The ST particles were introduced as a relative ratio (weight percent) of PVA. For example, 50 g/100 ml ST particles was mixed with 10 g/100 ml PVA to prepare PVA–ST blend films of 1/5 composition. The Me_2SO/H_2O composition was set to be 60/40 vol% to assure the significant drawability of PVA films on the basis of a report by Matsuo et al. [15]. The solutions were prepared by heating the well-blended polymer/solvent mixture at 105 °C for 40 min. The homogenized solution was poured into an aluminum tray kept at a temperature above 100 °C and then the tray was placed in a cold bath set at −30 °C or room temperature, thus generating a gel. The gels kept at the same temperature for 5 h were dried by evaporating solvents under ambient conditions. The dry gel film was cut into strips of length 25 mm and width 10 mm. The strip was clamped in a manual stretching device in such a way that the length to be drawn was 20 mm. The specimen was placed under nitrogen at 120 °C and elongated manually up to 5 times. Further elongation was done at 160 °C up to 8 times, since a suitable temperature to realize the facile drawability shifted to a higher value as the draw ratio increased.

The undrawn and drawn films were pretreated with hydrogen chloride vapor in a desiccator and subsequently the formalization of the pretreated specimens was done with formaldehyde vapor. Both chemical reactions were done at 83 °C for 12 h.

X-ray measurements were carried out with a 12-kW rotating-anode X-ray generator (Rigaku RAD-rA). Wide-angle X-ray diffraction (WAXD) patterns were obtained with a flat camera using Cu Kα radiation at 200 mA and 40 kV. The incident beam was monochromatized by a curved graphite monochrometer. The intensity distribution was measured using a step-scanning device at a step interval of 0.1°, each measurement being at a fixed time of 100 s, in the range of diffraction angles from 8° to 50°. WAXD patterns were obtained with a flat camera.

The complex dynamic tensile modulus was measured at 10 Hz over a temperature range from −150 to 300 °C using a viscoelastic spectrometer (VES-F) obtained from Iwamoto Machine Co. The length of the specimen between the jaws was 40 mm and the width was about 1.5 mm. During measurements, the specimen was subjected to a static tensile strain in order to place the sample in tension during the axial sinusoidal oscillation. The complex dynamic modulus was measured by imposing a small dynamic strain to ensure linear viscoelastic behavior of the specimen [16].

Scanning electron micrographs were obtained using a JSM-T300 instrument.

Results and discussion

X-ray diffraction intensity curves of ST films prepared by aqueous solution and Me_2SO/H_2O mixed solutions with compositions of 30/70 and 60/40 are shown in Fig. 1a. Of course, the intensity curves are given after corrections for solvent scattering, polarization, and absorption. Interestingly, the crystallinity is sensitive to the solvents. Namely, the crystallinity was the lowest for the specimen prepared from a solution with 60/40 composition assuring the greatest drawability of PVA dry gel films. This indicates that the mixed solvent with 60/40 composition used in the following experiments hampers the crystallization of ST. This means that the characteristics of ST prepared from Me_2SO/H_2O mixed solution with 60/40 composition is obviously different from those prepared using aqueous solution. The film prepared from aqueous solution is transparent and very stiff but any elongation could not be realized. On the other hand, the specimen prepared from Me_2SO/H_2O mixed solution with 60/40 composition is similar to opaque and brittle condensed

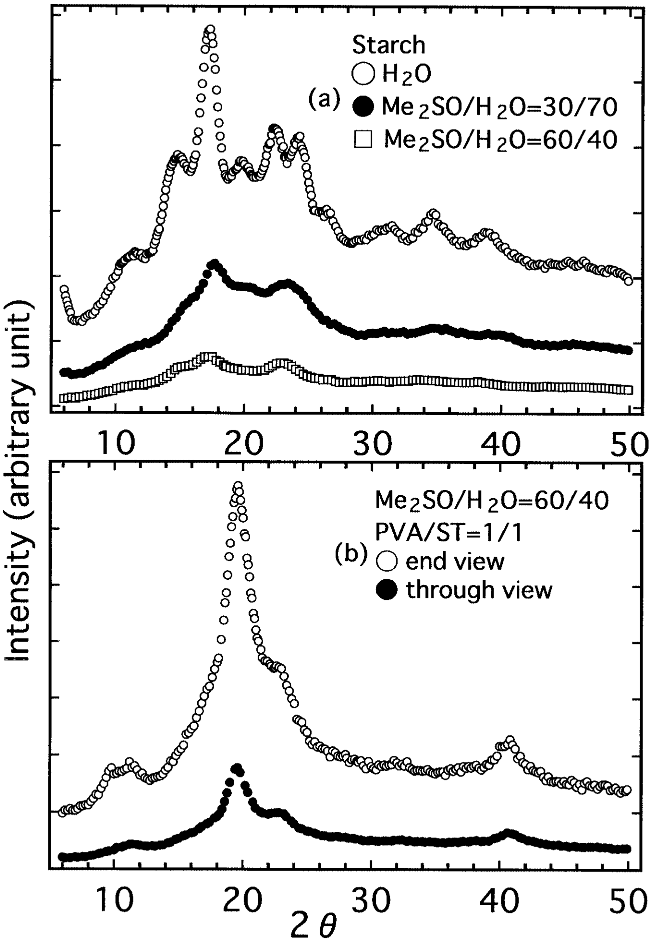


Fig. 1a, b X-ray diffraction intensity curve. **a** Starch (*ST*) films prepared using aqueous solution and dimethyl sulfoxide (*Me*$_2$SO)/H$_2$O mixed solutions with compositions 30/70 and 60/40. **b** Poly(vinyl alcohol) (*PVA*)–ST composite material prepared by gelation/crystallization from Me$_2$SO/H$_2$O mixed solutions with 60/40 composition at −30 °C

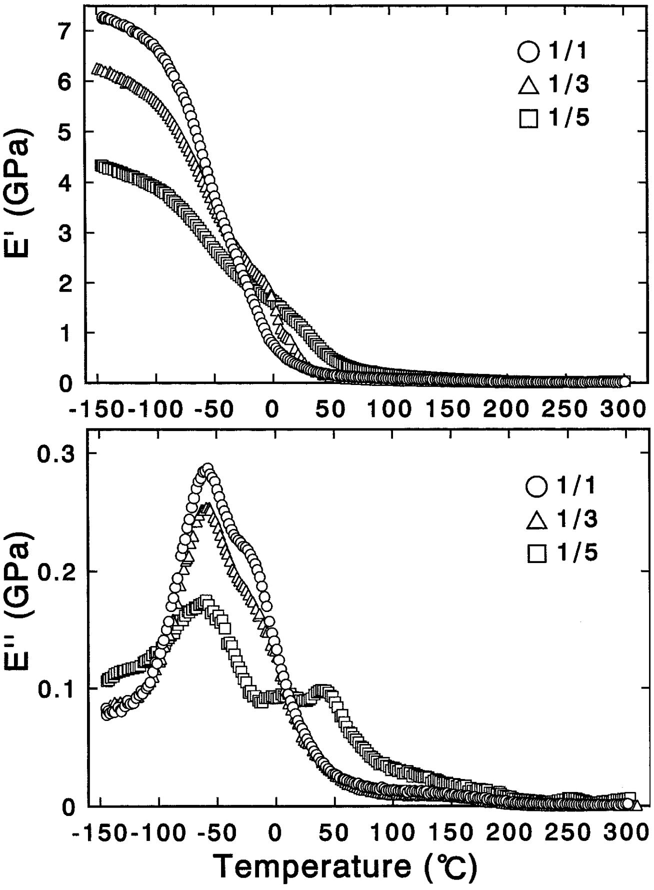


Fig. 2 Temperature dependence of the storage and loss moduli of dry gel films with different PVA/ST compositions

powder like single crystal mats of PE rather than a film.

X-ray diffraction intensity curves of PVA–ST composite material prepared by gelation/crystallization from Me$_2$SO/H$_2$O mixed solutions with 60/40 composition at −30 °C are shown in Fig. 1b. The PVA/ST composition is 1/1. Incidentally, the diffraction from the PVA films was almost the same as the diffraction of the 1/1 composite. All the diffraction peaks are only due to the contribution from PVA crystallites, since the reflection from ST is very weak. The following discussion is for the specimen prepared with the 60/40 mixed solvent.

The temperature dependence of the storage and loss moduli of dry gel films with different PVA/ST compositions is shown in Fig. 2. The gelation was done at 20 °C. The storage modulus decreases with increasing ST content. From preliminary experiments, the storage and loss moduli were found to be hardly affected by the gelation temperature. As shown in Fig. 2, the ST hampers the improvement of the storage modulus in spite of an elongation of 8 times. The loss moduli for the 1/3 and 1/1 compositions show a peak at −55 °C and a shoulder at −20 to 10 °C, respectively, while that for the 1/5 composition shows a peak at −55 °C and a broad peak at 40 °C. Judging from the mechanical relaxation of polyethylene [17], the peak appearing at lower temperature is thought to be due to the local dispersion concerning motion of side groups, while the peak or shoulder at higher temperature is due to the amorphous dispersion. Similar profiles have been confirmed for PVA dry gel films. The measurement of the storage and loss moduli of ST films was impossible because of the high brittleness. The local dispersion of the composite at −55 °C is hardly affected by the ST content but the peak becomes broader with increasing ST content. The appearance of the peak was observed at 40 °C for the 1/5 blend but was not observed for the 1/3 blend. The peak is probably due to the contribution from amorphous dispersion of PVA; however, this reason why this appeared only for the 1/5 blend still remains an unresolved problem.

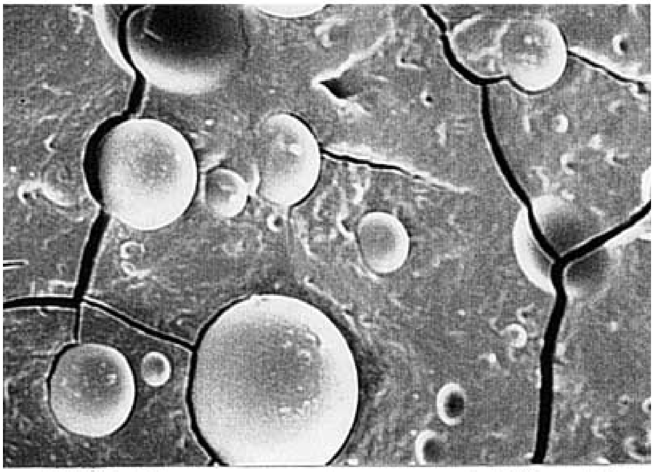
Incidentally, similar profiles of the storage and loss moduli were obtained for the specimens prepared by gelation at −30 °C, indicating that the viscoelastic properties of the blends is hardly affected by gelation temperatures from −30 to 20 °C. Accordingly, further experiments were done for the dry gel films prepared at 20 °C. To check the decrease in the storage modulus, the morphology of the blends was observed by scanning electron microscopy.

The scanning electron micrographs are shown in Fig. 3. Figure 3a and b shows the surface and edge of the 1/5 composite, respectively. Figure 3c is an enlargement of Fig. 3b, and is shown to demonstrate the existence of perfect spherulitic ST domains clearly. As shown in Fig. 3a, the ST could not be observed on the surface, indicating that the surface energy of PVA is much lower than that of ST. When the composite materials quenched by liquid nitrogen were broken, the spherulitic ST domains could be observed at the edge. These spherulitic ST domains with different radius are obviously not original ST particles with ellipsoidal shape. This is quite different from the PE–ST blend systems [11]. For PE–ST blend systems, the PE and ST were well blended in decalin at 130 °C. The ST particles were dispersed in PE solution without dissolution and the solution was quenched to room temperature to prepare gels. In this case, the original ST particles remained within the PE–ST blends. In contrast, the original ST particles in this experiment were dissolved but the radius of the spherulitic domains was much larger than that of the original ST particles. The appearance of the large spherulitic ST domains is due to the phase separation between ST and PVA. As discussed before, the ST sheet prepared using the 60/40 mixed solvent was similar to the condensed powder as discussed before and then the spherulitic ST domains seem to be composed of powder.

Because of incompatibility, cracks appear mostly on the boundary between the PVA medium and the ST domains. In some parts, the cracks break a ST domain (Fig. 3b) under the drying process. Even so, this specimen is tough enough to measure the temperature dependence of the storage and loss moduli shown in Fig. 2 with small external strain. The specimens with 1/3 and 1/5 compositions were broken at a strain higher than 5% and the tensile strength could not be obtained. For the 1/1 composition, the specimens could be elongated up to 8 times but the stress–strain curve could not be proposed because of the scattered values. In spite of the measurements for the same kind of specimens with $\lambda = 8$, some curves provided high stress and some curves low stress without statisitcal tendency.

Incidentally, similar spherulitic domains were observed for the 1/3 compositions. However, no large


(a) Surface


(b) Edge

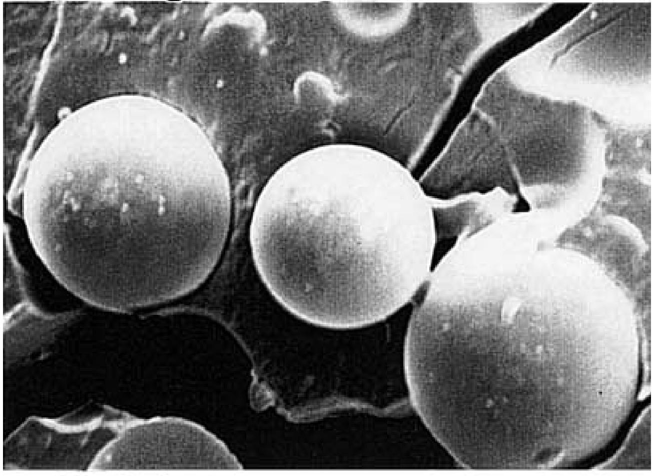

(c) Edge

Fig. 3a–c Scanning electron micrographs of composite materials. **a** Surface of the 1/5 composite, **b** edge of the 1/5 composite, and **c** edge of the 1/5 composite (enlargement of (b)) spherulitic domains could be observed for the 1/1 blend and small ST domains with irregular shape were dispersed in PVA medium.

A Scanning electron micrograph for a drawn blend ($\lambda = 8$) with a 1/1 composition is shown in Fig. 4. The fibrous texture oriented parallel to the stretching direction tends to form a relatively smooth surface in places. This behavior is quite different from PE–ST drawn blends, where a number of ST particles existing in gaps between the oriented filaments hamper the formation of a smooth surface. Of course, the very small ST domains observed on the surface are not original ST particles, as discussed before. After the mixing at the molecular level, it is evident that phase separation of ST and PVA molecules occurred under the cooling process to room temperature.

The solubility of ST particles within the blends, in which the specimens were immersed in water at 20 °C and then 83 °C for the times indicated is shown in Fig. 5. W_d is the weight of the original dry blends and W_0 is the weight of the blends vacuum-dried after removal from the water bath. The value $(W_d - W_0)/W_d$ increases with time, indicating that ST domains were dissolved in water by penetration of water molecules into the PVA medium. The solubility becomes significant for the 1/5 blend in an undrawn state and for the 1/1 blend with $\lambda = 8$. Especially drastic solubility occurred at 83 °C. Even in water at 23 °C, the solubility of the blend film buried in soil provides a serious problem for biodegradation of the blends, if most of the ST domains are caused to flow out from the blend by heavy rain and only PVA is maintained as a residual trace in the soil.

To avoid this accident, formalization was carried out to formulate cross-linking of PVA chains. The results are shown in Fig. 6. Significant improvement can be realized by the cross-linking of PVA chains. For the 1/1 blend, the amount of ST dissolved in water at 20 °C was less than 3% for the undrawn state and was 20% for the drawn film, while for the 1/5 undrawn blend, it was less than 20%. The water content relating to the biodegradation in soil is obviously different from such a serious experimental condition that several pieces of blend film were immersed in a water bath. The result in Fig. 6 indicates that most of the ST domains were maintained within the blend buried in soil.

Incidentally, when the specimens were immersed in a hot water bath at 83 °C, the amount of dissolved ST is more than 40% for the 1/1 blend with $\lambda = 8$ and the 1/5

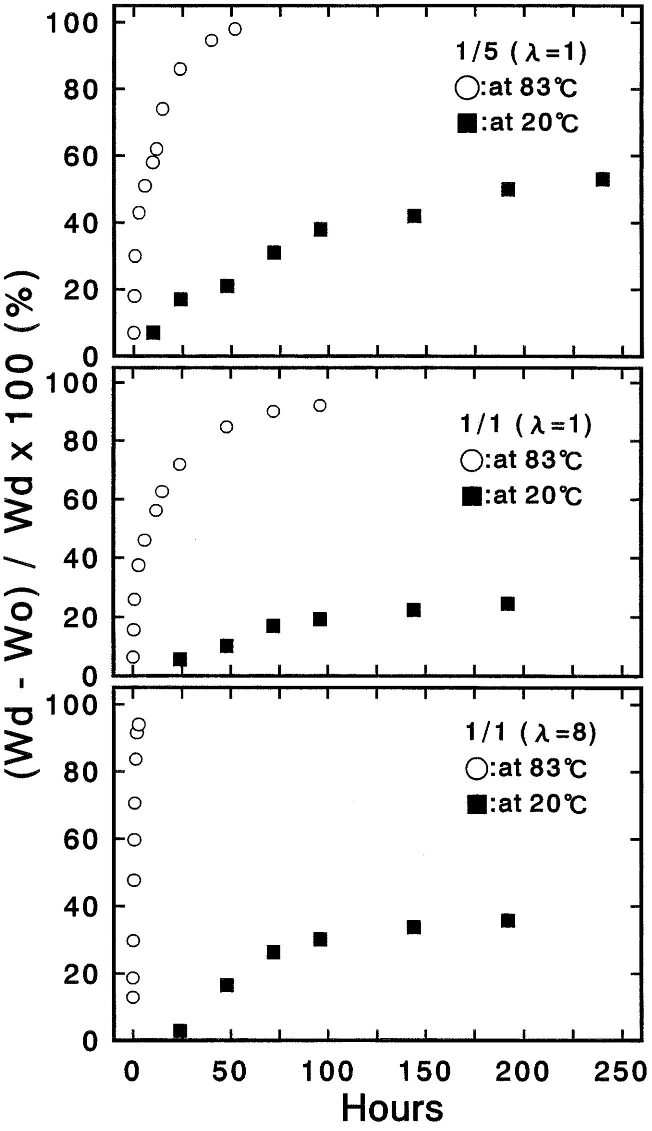


Fig. 5 Change in weight of the nonformalization blends treated with water at 20 and 83 °C measured as a function of time, where W_d is the weight of the dry film and W_0 is the weight of film vacuum-dried after removal from the water

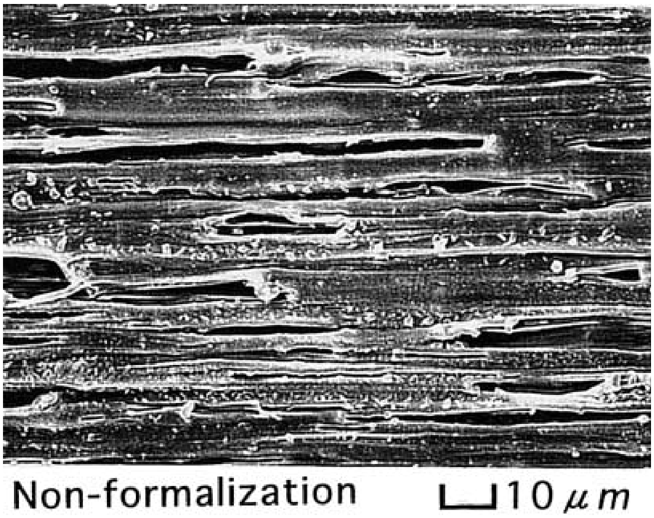


Fig. 4 Scanning electron micrographs for a drawn blend ($\lambda = 8$) with 1/1 composition

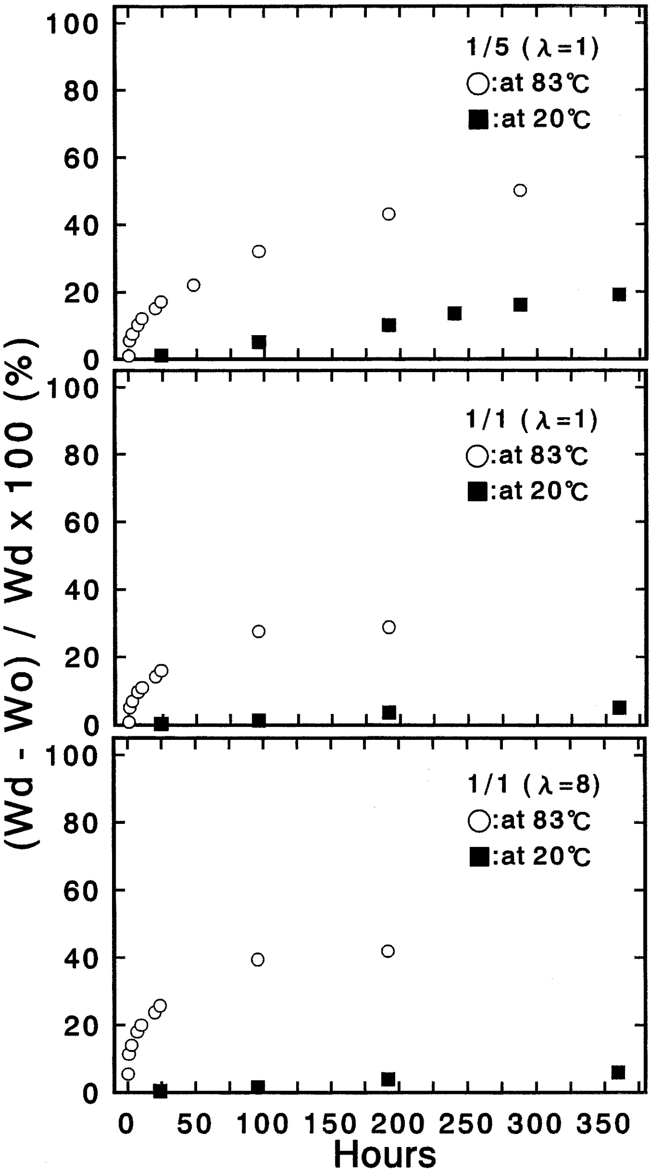


Fig. 6 Change in weight of the formalization blends treated with water at 20 and 83 °C measured as a function of time

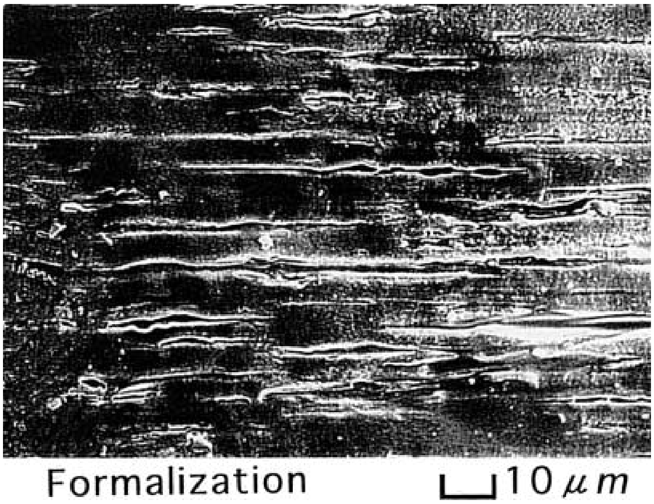


Fig. 7 Scanning electron micrographs for the formalization blend with 1/1 composition drawn up to $\lambda = 8$

blend with $\lambda = 1$, while the amount of dissolved ST of the 1/1 blend with $\lambda = 1$ was about 30%. In comparison with the solubility in Fig. 5, much improvement was established by the formalization.

The question arises as to whether the mechanical properties and thermal dimensional stability of the formalization specimens become worse or not than those of nonformalization ones. To check them, a series of related experiments were carried out.

Scanning electron micrographs for formalization blend (the 1/1 composition) with $\lambda = 8$ are shown in Fig. 7. The elongation was done after the formalization. In comparison with the nonformalization blend in Fig. 4, the fibrous texture oriented parallel to the stretching direction also tends to form a relatively smooth surface in places and interestingly the gaps between the oriented fibrils become narrower, indicating the shrinkage of the width of the specimen. Furthermore, the number of small ST domains becomes less. The disappearance suggests that the ST particles moved from the surface to the inner part by the narrowing of cracks and consequently most of ST domains on the surface could not be observed under scanning electron microscopy.

The temperature dependence of the storage and loss moduli of dry gel films with the 1/1 blend are shown in Fig. 8. For the undrawn films, the storage modulus of the formalization blend at temperatures above −80 °C is higher than that of the nonformalization blend. For the drawn films with $\lambda = 8$, the storage modulus of the formalization blend at temperatures above −5 °C is higher than that of the nonformalization blend. This means that the mechanical properties of the formalization blends become better at conditions utilized for commercial materials. The value of the specimen with $\lambda = 8$ at 20 °C was about 2 GPa. The apparent small difference of the storage moduli between undrawn and drawn blends is confirmed for nonformalization and formalization blends, although the X-ray diffraction patterns from the drawn blends provided preferential orientation of PVA crystallites with respect to the stretching direction. Here we must emphasize that at temperatures above −5 °C, the storage modulus of drawn films measured after removing ST domains is about more than 10 times the values in Fig. 8. The removal was done in hot water at 100 °C. This indicates that the existence of ST domains irrespective of mechanical properties causes the drastic decrease in the apparent storage modulus because of a drastic increase

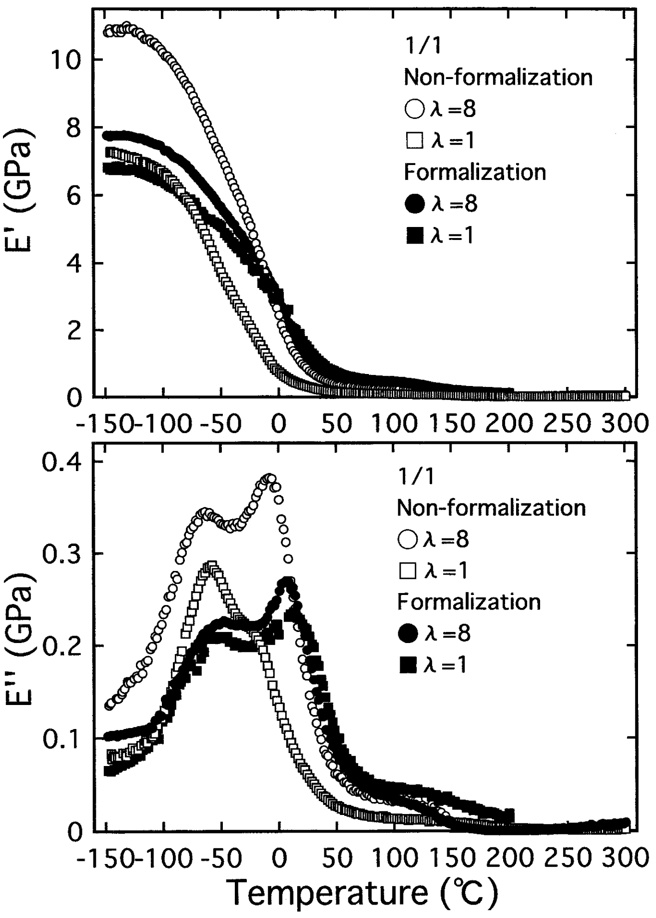


Fig. 8 Temperature dependence of the storage and loss moduli of nonformalization and formalization blends with 1/1 composition

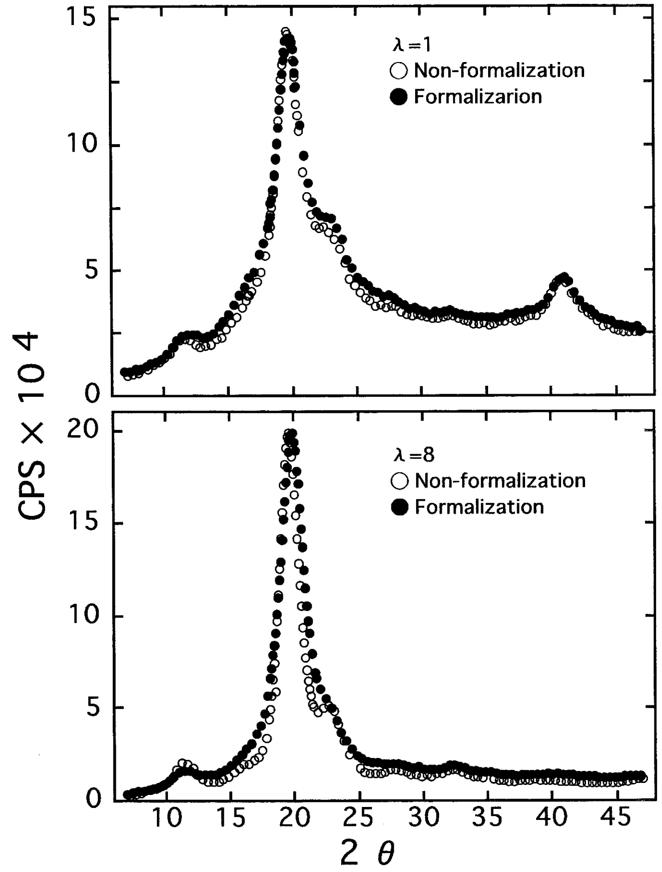


Fig. 9 X-ray diffraction intensity curves of 1/1 blends with nonformalization and formalization

in the cross-sectional area. For the corresponding loss modulus, a distinct peak appeared at 10 °C for the formalization blend with $\lambda = 1$. This is probably due to the growth of the shoulder of the nonformalization blend in Fig. 2 and the reason still remains an unresolved problem.

X-ray diffraction intensity curves of the 1/1 blends with nonformalization and formalization blends are shown in Fig. 9. For the undrawn blends, the intensity magnitudes of the two blends are the almost same, indicating no change in crystallinity as a result of formalization. For the drawn blend, the shoulder at 20 °C due to the reflection of the (200) plane disappeared and the half-width of the overlapped peak of the (110) and $(1\bar{1}0)$ planes becomes broader as a result of formalization, indicating slight decreases in crystal size and crystallinity. The same tendency was also confirmed for PVA homopolymers.

The change in stress against temperature measured for the 1/1 blend is shown in Fig. 10. During the measurements, the specimens were kept at a constant length. For the nonformalization blend ($\lambda = 1$), the stress increases drastically up to 80 °C and tends to decrease up to 120 °C. With further increasing temperature, the stress increases. A similar tendency was observed for the formalization blend but the magnitude was much smaller; namely, a very slight increase in stress up to 120 °C and subsequently a very slight decrease up to 160 °C and an increase with further increasing temperature were observed. In contrast, the stress increases with increasing temperature for the drawn blends ($\lambda = 8$). This is due to the considerable rubber elasticity of PVA chains associated with active chain mobility at elevated temperature. Anyway, it may be noted that the increase in stress for the formalization blend at elevated temperature is much slower than that for the nonformalization blend, indicating better thermal dimensional stability. The cross-linking of PVA chains by formalization hampers active PVA chain mobility to form random coils at elevated temperature.

Incidentally, the cross-linking could not be detected by Fourier transform IR measurements. The spectrum of non-cross-linking PVA film showed a very complicated profile in comparison with the normal profile published in textbooks, indicating a residual trace of

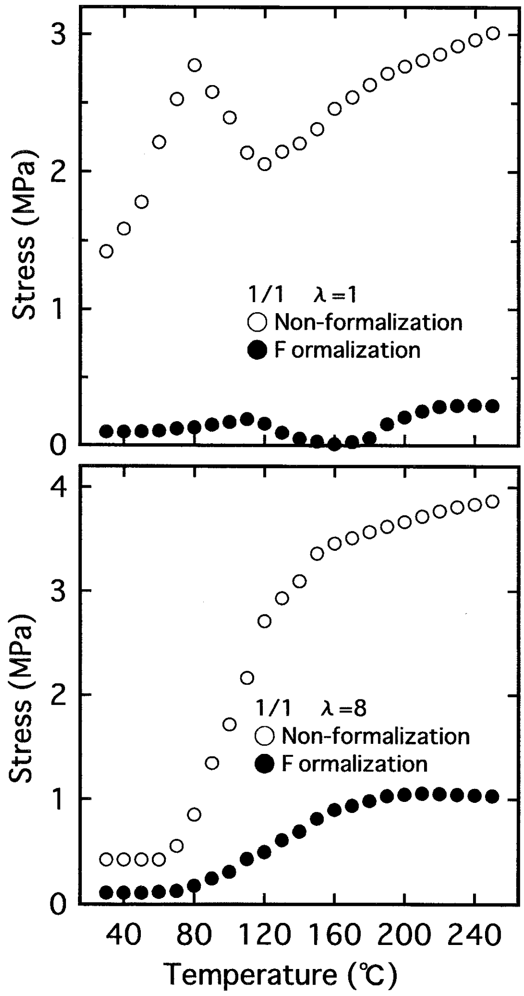


Fig. 10 Change in stress against temperature for the nonformalization and formalization blends at a constant length

mixed solvent of Me_2SO and H_2O. The spectra of the cross-linked and non-cross-linked PVA films were the same without showing any new absorption peaks due to chemical change by the cross-linking. Of course, the difference for PVA–ST blends could not be detected. This means a very small cross-linking density within the blends and PVA films, although formalization caused significant effects on the mechanical property and solubility of ST from the blends.

A series of the formalization blends were buried in soil for several months. Under scanning electron microscopy, the ST domains disappeared perfectly and some parts of blend films disappeared. However, the question arises as to whether the drastic biodegradation effect of the PVA medium could be confirmed or not. Even so, it was obvious that the biodegradation effect is promoted much more than that of polyethylene [11]. To derive conclusive evidence, further experiments must be carried out by using blends buried in soil for more than 2 years. Another important problem was that mud from the soil adhered to the specimens. In the biodegradation experiment, it was more difficult to remove the mud from the PVA–ST specimens in comparison with PE–ST specimens. A suitable method to remove the mud from the specimen must be considered to estimate the biodegradation effects quantitatively.

Conclusion

Ultradrawing of PVA–ST blends was prepared by gelation/crystallization from semidilute solutions in Me_2SO and water mixtures. The content of mixed solvent was 60/40. The PVA/ST compositions chosen were 1/1, 1/3, and 1/5. Spherulitic ST domains with different radii could be observed. These spherulitic domains were not original ST particles with ellipsoidal shape but the aggregation of powders. Such spherulitic domains were formed by phase separation of PVA–ST mixed solution in the gelation process. Elongation up to 8 times could be done for the 1/1 blend but any elongation was impossible for blends whose ST content was beyond 50%. When the blends were immersed in water at 20 or 83 °C, the solubility becomes significant for the 1/5 blend in an undrawn state and for the 1/1 blend with $\lambda = 8$. To avoid this phenomenon, formalization was carried out to formulate cross-linking of PVA chains. Significant improvement could be realized by the cross-linking of PVA chains. For the 1/1 blend, the amount of ST dissolved in water at 20 °C was less than 3% for undrawn and drawn films. The storage modulus of the formalization blend at temperatures above −80 °C is higher than that of the nonformalization blend in an undrawn state. For the drawn films with $\lambda = 8$, the storage modulus of the formalization blend (the 1/1 composition) is slightly higher than that of the nonformalization blend at temperatures above −5 °C. The Young's modulus of the drawn films was 2 GPa at 20 °C. The formalization blend provided better thermal dimensional stability.

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