

Molecular Composite of Lignin: Miscibility and Complex Formation of Organosolv Lignin and Its Acetates with Synthetic Polymers Containing Vinyl Pyrrolidone and/or Vinyl Acetate Units

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ABSTRACT: Binary blends and pseudo-complexes of organosolv lignin (OSL) or its acetate (OSL-Ac) with synthetic polymers including poly(vinyl acetate) (PVAc), poly(*N*-vinyl pyrrolidone) (PVP), and poly(*N*-vinyl pyrrolidone-*co*-vinyl acetate) (P(VP-*co*-VAc)) were prepared by casting from mixed polymer solutions in *N,N*-dimethylformamide as good solvent and by spontaneous coprecipitation from solutions in tetrahydrofuran (THF) as comparatively poor solvent. Thermal analysis by differential scanning calorimetry showed that OSL was not miscible with PVAc; however, OSL(-Ac) was miscible with PVP to form homogeneous blends irrespective of the degree of acetylation of OSL. OSL formed homogeneous blends with P(VP-*co*-VAc) with ≥ 30

mol % of VP contents. Fourier transform infrared spectra measurements for the miscible blends of OSL/PVP revealed the presence of hydrogen bonding interactions between hydroxyls of OSL and carbonyls of VP units. However, there was no evidence for the development of the hydrogen bonding in miscible blends of fully acetylated OSL with PVP. For complexes via THF solutions, its formation was found to be primarily due to a higher frequency of hydrogen bonding interactions. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2063–2070, 2012

Key words: organosolv lignin; poly(*N*-vinyl pyrrolidone); blends; complex; miscibility

INTRODUCTION

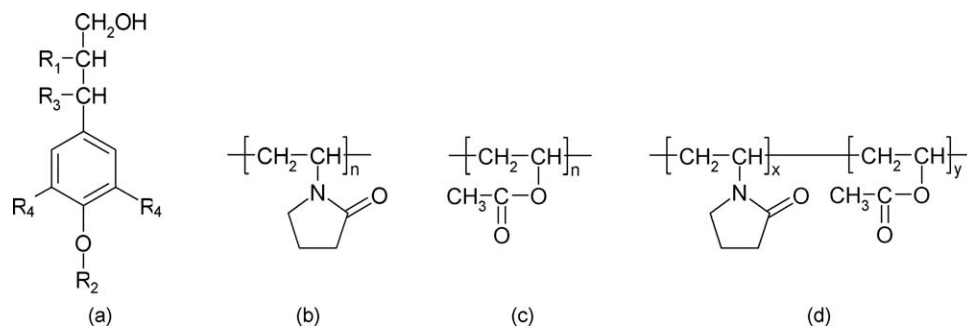
Currently, studies on bioethanol production from lignocellulosics are being actively pursued.^{1–4} Irrespective of the bioethanol manufacturing process, lignin is inevitably produced as a consequence of the saccharification of the cellulosic components of lignocellulosics. However, in the present circumstances, this lignin byproduct is considered merely as a heat resource for the process. Actually, the utilization of lignin as a solid material is constrained by poor film formability and less thermal moldability due to its molecular architecture and intermolecular interactions in itself. Blending of lignin with other polymers is a possible way to modify the thermal and other physical properties of the target lignin and to obtain new polymeric materials having wide-ranging properties.^{5–12}

However, it is generally difficult to prepare miscible blends because of the small contribution of the mixing entropy. Therefore, in most cases, certain attractive intermolecular interactions between the component polymers should be adopted to attain miscibility or practically good compatibility. Recently, some research groups have focused on the intermolecular interactions to obtain lignin-based polymer blends, for example, an ionic interaction,⁶ hydrogen bonding attraction,^{7,8} and a specific structure of the counterpart polymer^{10–12} were used to enhance the miscibility or compatibility of two constituent polymers.

The current study provides a guide for the material design of lignin via intermolecular interaction by means of an example of an intimate microcomposite of lignin/synthetic polymer to diversify the microcomposites resulting in wood-related industries. Organosolv lignin (OSL) is used as the lignin sample. OSL is produced as a solute byproduct during the ethanol organosolv pulping process.¹³

Miscibility characterization is performed for the binary blends of OSL with comparatively flexible, noncrystalline vinyl polymers. Poly(*N*-vinyl pyrrolidone) (PVP), poly(vinyl acetate) (PVAc), and poly(*N*-vinyl pyrrolidone-*co*-vinyl acetate) (P(VP-*co*-VAc))

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Scheme 1 Chemical structures of (a) a typical phenyl propane unit in OSL (R_1 and R_2 represent H or lignin; R_3 represents H, OH, or lignin; and R_4 represents H or OCH_3), (b) PVP, (c) PVAc, and (d) P(VP-*co*-VAc).

are selected as the mixing partners for OSL. In fact, a crosslinked product of PVP can be used as a fining agent to remove polyphenolic impurities by absorption in beverage industries.¹⁴ For DNA purification, PVP is also exceptionally good at absorbing polyphenols, which are common in many plant tissues and can deactivate proteins if not removed and therefore inhibit many downstream reactions like PCR.¹⁵ Because of these factors, we initially expected that technically isolated lignin materials could also interact with PVP.

Actually, there have been reports for blends of PVP¹⁶ and PVAc¹⁷ with sugarcane bagasse lignin extracted with formic acid from a sugar and alcohol factory residue. However, in these systems, lignin contents in the blends were low (≤ 15 wt %) and they have not yet led to clear miscibility judgments. In the current work, different conditions for mixing OSL with PVP, involving wide-ranging blend compositions, selections of the solvent, and the degree of acetylation of OSL as well as of the VP/VAc composition in the P(VP-*co*-VAc), were examined to clarify the effect of molecular structure on the miscibility attainment. Measurements including differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) were performed to elucidate the emergence of the intermolecular interaction between OSL and PVP.

EXPERIMENTAL SECTION

Materials

OSL was purchased from Aldrich Chemical (WI, USA). The vinyl polymers used as mixing partners for OSL were PVP, P(VP-*co*-VAc), and PVAc. The PVP sample was purchased from Nacalai Tesque (Kyoto, Japan); its nominal weight-average molecular weight (M_w) was 24,500. Three P(VP-*co*-VAc) samples were obtained from Polysciences, with nominal VP/VAc (mol/mol) compositions of 70/30, 50/50, and 30/70, respectively; the corresponding copolymer samples were designated as P(VP-*co*-VAc)7030, P(VP-

co-VAc)5050, and P(VP-*co*-VAc)3070, respectively. The M_w values of these samples were in the range of 25,000–30,000, and the molecular weight distributions were about 5.5–6.0, as estimated by gel permeation chromatography (mobile phase, *N*-methyl pyrrolidone containing 10 mM LiBr; calibration, monodisperse polystyrene standards). The PVAc sample was purchased from Nacalai Tesque; its nominal number-average molecular weight (M_n) is 35,000. The chemical structures of OSL, PVP, PVAc, and P(VP-*co*-VAc) are illustrated in Scheme 1. All the solvents and chemicals used in this study were purchased from Wako Pure Chemical Industries (Osaka, Japan); these were all guaranteed as reagent grade and were used without further purification.

Preparation of acetylated OSL

A 3 g sample of OSL was added to 30 mL of pyridine. Subsequently, 45 mL of acetic anhydride and 1.5 g of 4-dimethylaminopyridine were added to the OSL solution. The mixture was then heated to 100°C and maintained at this temperature for 3 h. The above procedure was conducted with vigorous stirring. The acetylated product (OSL-Ac) was recovered by precipitation in water, washed successively with water, and dried at 40°C *in vacuo* for 48 h. By this procedure, 60% acetylated OSL was obtained, designated as OSL-Ac60. Subsequently, 1 g of this product was further acetylated with 15 mL of acetic anhydride and 0.5 g of 4-dimethylaminopyridine in 10 mL of pyridine to complete the substitution. Purification and drying of the product [100% acetylated OSL (OSL-Ac100)] were performed using a sequence of procedures similar to that mentioned above.

Characterization of OSL

Methoxyl ($-\text{OCH}_3$) group content in OSL was determined by the modified method of Viebock and Schwappach.¹⁸ Elemental analysis was conducted at the Natural Science Center for Basic Research and Development, Hiroshima University. For descriptive

TABLE I
Characterization of OSL Used in This Work

Sample	Functional groups per PPU					M_w (10^{-3})	M_w/M_n
	Total OH	AlOH	ArOH	$-\text{OCH}_3$	ArH		
OSL	1.23	0.61	0.62	0.83	2.92	3.38	3.52

purpose, the phenyl propane unit (PPU) formulae of the OSL used was determined to be $\text{C}_9\text{H}_{8.7}\text{O}_{2.6}(\text{OCH}_3)_{0.83}$, even though technical lignins are chemically denatured by various types of reactions, such as ethylation and condensation for the organosolv pulping process.¹⁹ The PPU molecular weight of the OSL was 184 g/mol.

Functional group contents of OSL and the degree of acetylation for OSL-Ac were further determined by FTIR and $^1\text{H-NMR}$ spectroscopy. FTIR spectra were obtained by using a PerkinElmer Spectrum GX spectrometer. A standard KBr pellet method was used for all the measurements. $^1\text{H-NMR}$ spectra (300 MHz) were measured at 20°C for OSL and OSL-Ac by using a Varian INOVA 300 apparatus. A pulse width of $3.0\ \mu\text{s}$ was used and 256 scans were conducted. Approximately 100 mg of OSL or OSL-Ac was dissolved in 1 mL dimethyl sulfoxide ($\text{DMSO-}d_6$, 99.9% deuterated, 0.05% tetramethylsilane; Cambridge Isotope Laboratories) and left overnight over molecular sieves to reduce water contamination. Chemical shift assignments were taken from the literature.^{20–23} Functional groups present in OSL were determined by $^1\text{H-NMR}$ spectroscopy using dichloromethane as internal reference. Aromatic protons (ArH, 8–6.2 ppm) were used as a reference. Interference occurred between aromatic alcohol (ArOH) and aldehyde (CHO) proton signals in the 8–11 ppm range. After obtaining the initial spectrum of OSL in $\text{DMSO-}d_6$, by an addition of 20 vol % D_2O , an exchange of the ArOH protons with a deuterium nucleus of D_2O occurred, whereas the CHO protons were not substituted by deuterium.^{20,24} Therefore, a subtraction of the signal with D_2O from the signal with the plain $\text{DMSO-}d_6$ canceled out the CHO proton contribution, then the ArOH content could be estimated. Aliphatic alcohol (AlOH) content in OSL was calculated from the total and aromatic hydroxyl conversions of acetylated OSL. The extent of acetylation of OSL-Ac was determined from the acetyl protons (1.6–2.5 ppm). FTIR measurements demonstrated that the bands of hydroxyls for OSL-Ac100 disappeared, revealing that this acetylated product is fully substituted one.

The molecular weights of OSL and its esters were determined by using a TOSOH HLC-8220 gel permeation chromatograph equipped with a refractive index detector and two TSK-GEL SuperAWM-H columns connected with each other. The measurement

was conducted by using *N*-methylpyrrolidone containing 10 mM LiBr as the mobile phase at a flow rate of 0.3 mL/min. The concentration of the test sample was 1.0 g/L, and the quantity of injection was 20 μL . The system was calibrated with monodisperse polystyrene standards. The results of the quantifications are summarized in Table I.

Preparation of blend samples

Polymer blends of OSL(-Ac) with vinyl polymers were prepared in film form from mixed polymer solutions by the solvent evaporation process. *N,N*-Dimethylformamide (DMF) was selected as the common solvent. About 1.0 wt % solutions of OSL(-Ac) and vinyl polymer were prepared separately and mixed with each other in the prescribed proportions. After stirring for 24 h at 25°C , each mixed solution (transparent but brown) was poured into a Teflon tray, and a film sheet was prepared by solvent evaporation at 50°C under reduced pressure ($<10\ \text{mmHg}$).

Pseudo-complexes of OSL(-Ac)/vinyl polymer were prepared in powder form via mixing of two polymer solutions with tetrahydrofuran (THF) as a common solvent. A 0.4 wt % solution of OSL(-Ac) and those of the respective vinyl polymers were prepared separately, and the pairing polymer solutions were mixed with each other in the desired proportions to give a brown precipitate spontaneously. After stirring over a period of 24 h at 25°C , each suspension was centrifuged at 2500 rpm for 15 min and washed with THF several times. The precipitates thus obtained were then dried at 40°C *in vacuo* for 3 days.

Measurements

FTIR spectroscopy and elemental analysis of blend films and powdery precipitates were obtained by means of the method described above.

DSC measurements were performed using a Perkin-Elmer Pyris 1 DSC. The measurements were conducted using 5 mg samples under a nitrogen atmosphere after calibrating the temperature readings with an indium standard. The samples were first heated from -50 to 220°C at a scanning rate of $20^\circ\text{C}/\text{min}$ (first heating scan) and then immediately quenched to -50°C at a rate of $80^\circ\text{C}/\text{min}$. The second heating scans were run from -50 to 220°C at a scanning rate of $20^\circ\text{C}/\text{min}$ to record stable thermograms.

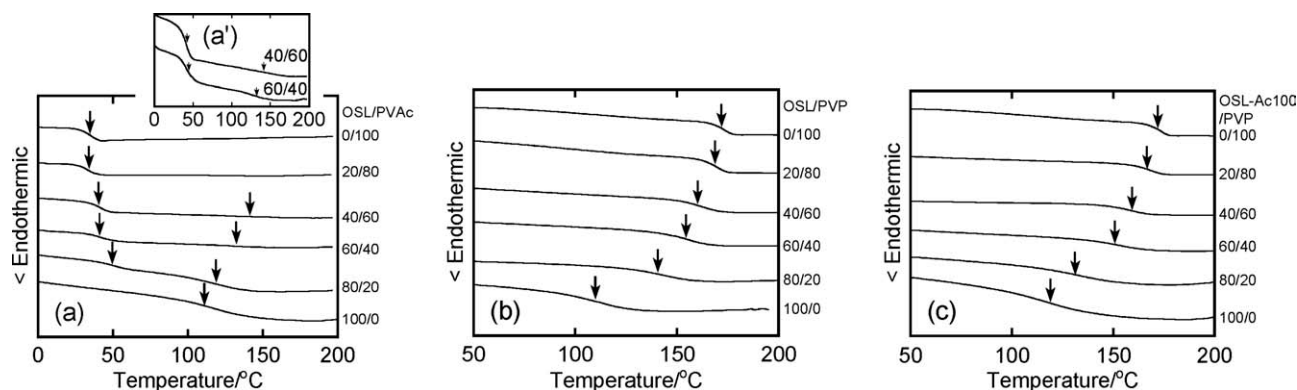


Figure 1 DSC thermograms (second heating scan) obtained for (a) OSL/PVAc [(a') shows the data for 40/60 and 60/40 blends on an enlarged scale], (b) OSL/PVP, and (c) OSL-Ac100/PVP blends. Arrows indicate T_g positions.

RESULTS AND DISCUSSION

OSL/PVAc blends

As-cast films of OSL/PVAc blends from the mixed polymer solutions in DMF were visually homogeneous, but became browner with an increase in the OSL content. The visual inspection provided no indication of phase separation in any of the blends.

Polymer-polymer miscibility is commonly estimated by the determination of the glass transition temperature (T_g) of the blends. If any sample of a binary polymer system exhibits a single glass transition between the T_g values of both the components and a composition-dependent shift in T_g of the blend is clearly observed, then the system can be regarded as a highly miscible one.

Figure 1 displays selected data of DSC thermograms obtained for a series of OSL/PVAc samples. In the DSC curve of PVAc alone, a clear baseline gap reflecting the glass transition is observable. From the midpoint of the discontinuity in heat flow, the T_g of the unblended PVAc was evaluated to be 34°C. The other component OSL also exhibits an explicit signal of glass transition in the thermogram, and its T_g was determined to be 110°C. Concerning the blends of these polymers, two independent glass transitions were clearly detected for OSL/PVAc = 40/60, 60/40, and 80/20 (wt/wt), and the other composition showed only the glass transition of PVAc ingredient at almost the same positions observed for the unblended sample, as demonstrated in this figure. From these results, it is seen that the polymer pair of OSL and PVAc is immiscible.

OSL(-Ac)/PVP blends

OSL(-Ac)/PVP blend films were also homogeneous to the naked eye over the whole range of composition for each blending pair. DSC thermograms of selected blends of OSL with PVP are illustrated in Figure 1(b). The plain PVP sample exhibits a clear

baseline gap due to glass transition with the midpoint at 172°C. In contrast to the result obtained for the OSL/PVAc system [Fig. 1(a)], the thermograms compiled in Figure 1(b) for the OSL/PVP blends definitely indicate a single T_g that shifts to the lower temperature side along with the increase in the OSL content. The detection of the single T_g varying in location with composition allows us to conclude that the OSL is capable of forming a miscible amorphous phase in the binary blends with PVP.

In Figure 2, FTIR spectra of selected OSL/PVP samples are shown on an enlarged scale for two regions of (a) O—H and (b) C=O stretching vibrations. As can be seen in Figure 2(a), the unblended OSL provides a major peak with its maximum at 3418 cm^{-1} , which is associated with hydroxyl groups. PVP homopolymer also demonstrates O—H stretching band of the adsorbed water because of its hygroscopic nature. For the OSL/PVP blend samples, the 3418 cm^{-1} band of OSL shifted to a lower wavenumber position. In addition, a prominence around the band maximum was observed for PVP-rich compositions. By the addition of excess amounts of PVP, the

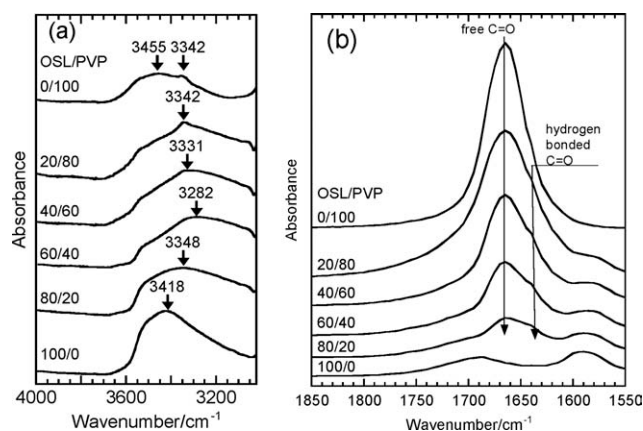


Figure 2 FTIR spectra of OSL, PVP, and their blends in the frequency regions of (a) O—H and (b) C=O stretching vibrations.

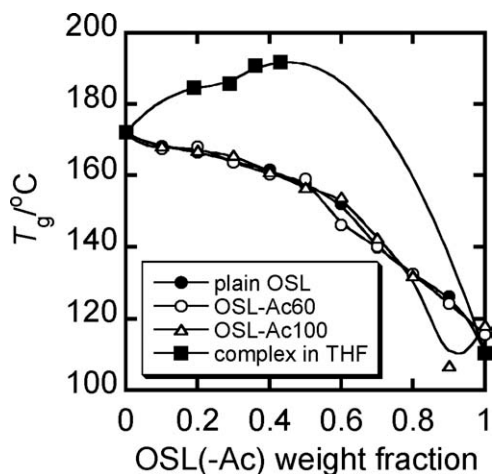


Figure 3 T_g versus composition plots for blends of OSL, OSL-Ac60, and OSL-Ac100 with PVP, together with the data for OSL/PVP complexes.

O—H stretching shifted to higher wavenumber and got close to the band of PVP homopolymer.

On the other hand, as shown in Figure 2(b), the plain PVP sample exhibits an absorption peak with its maximum at 1665 cm^{-1} . This absorption signal is assigned to the stretching vibration of C=O group in the pyrrolidone ring. The band at 1685 cm^{-1} for plain OSL may principally indicate the presence of C=O bond of Hibbert's ketones formed by organosolv pulping process. When OSL was added to PVP, a new shoulder corresponding to hydrogen-bonded C=O appeared at $\sim 1635\text{ cm}^{-1}$. The shoulder shifted to a lower frequency and became conspicuous with an increase in OSL content in the blend. These low-frequency shifts for both the O—H and C=O bands can be ascribed to the formation of intermolecular hydrogen bonding in the blends, as extensively observed in other blend systems.^{25,26} Thus, the principal driving force for the miscibility attainment for the OSL/PVP system is hydrogen bonding.

Figure 3 shows T_g versus composition plots collected for a series of OSL(-Ac)/PVP blends prepared with different degrees of acetylation (0, 60, and 100%) for the OSL constituent. Looking over the data depicted here, we can readily see the presence of a single glass transition in all the blend samples. The detection of the single T_g varying in location with composition allows us to conclude that the OSL(-Ac) samples are all miscible with PVP.

It is noteworthy that a miscibility attainment was confirmed even in the characterization for a series of fully acetylated OSL (OSL-Ac100)/PVP blends [their DSC thermograms are shown in Fig. 1(c)]. As has been described above, the miscibility characteristics are primarily related to hydrogen bonding for the blends containing OSL. This factor can be applicable for the blends containing OSL-Ac60 having hydroxyl groups, but not for those of OSL-Ac100.

Figure 4 illustrates the FTIR spectra of PVP and its blends with OSL-Ac100 in the range of $1550\text{--}1750\text{ cm}^{-1}$. In this region, OSL-Ac100 is characterized by bimodal bands centered at 1770 and 1740 cm^{-1} , which could be the bands of C=O stretching vibration for the acetate of phenolic and alcoholic hydroxyl groups, respectively. On the other hand, pure PVP provided a band of $>\text{C}=\text{O}$ stretching vibration at 1665 cm^{-1} , as has been pointed out above. On adding OSL-Ac100, this band was observed to shift to a higher frequency by 15 cm^{-1} when OSL-Ac100 content was 80%, suggesting the significant change of the intermolecular (or intramolecular) interactions due to blending. It should be noted that this high-frequency shift could not be interpreted as the formation of intermolecular hydrogen bonding in the blends. In this system, several kinds of intermolecular and intramolecular interactions could be involved, including P- π conjugation associated with amide functional groups of PVP²⁷ and the dipole-dipole interactions between carbonyl groups of PVP and OSL(-Ac). The inclusion of miscible OSL-Ac100 possibly brings about the dissociation of PVP chains. As a consequence, the carbonyl stretching vibration of PVP will shift to a higher frequency.

OSL/VP-containing copolymer blends

On visual inspection, cast films of OSL/P(VP-co-VAc) blends also showed a homogeneous appearance irrespective of the VP/VAc ratio of P(VP-co-VAc); the

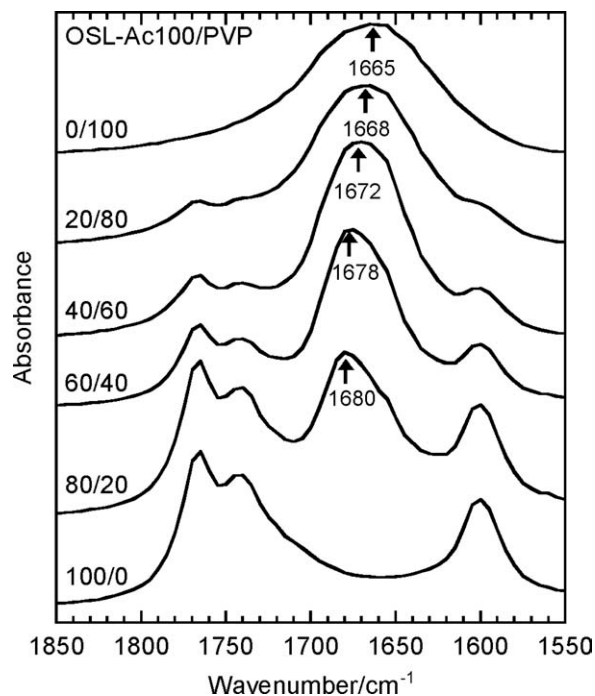


Figure 4 FTIR spectra of OSL-Ac100, PVP, and their blends in the frequency regions of C=O stretching vibration.

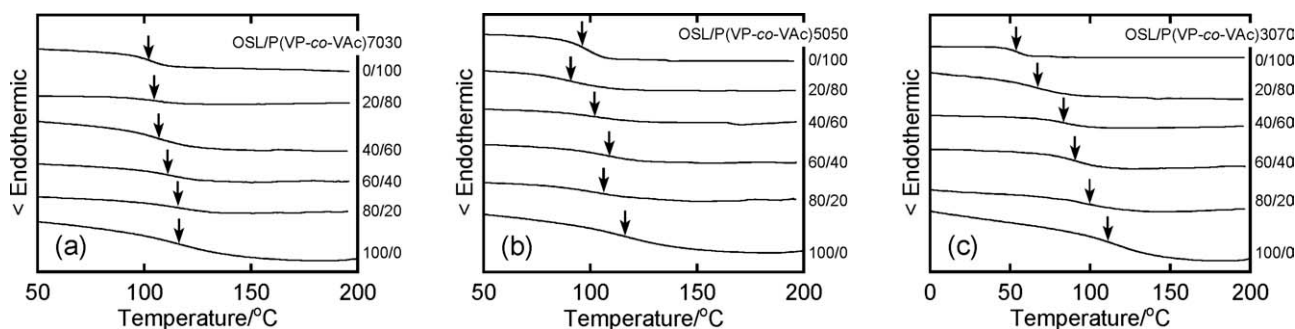


Figure 5 DSC thermograms (second heating scan) obtained for OSL blends with (a) P(VP-co-VAc)7030, (b) P(VP-co-VAc)5050, and (c) P(VP-co-VAc)3070. Arrows indicate T_g positions.

situation was almost comparable with that of the cast films of the corresponding OSL blends with PVP.

The miscibility behavior of this blend system can be presumed to be significantly affected by the copolymer composition. Figure 5 shows selected DSC thermograms for three series of OSL/P(VP-co-VAc) blends with different VP/VAc compositions in the copolymer component. As can readily be seen from the figure, the T_g s of both the component polymers were so close to each other that it was somewhat difficult to discriminate whether a single glass transition was truly detected or not. However, even for the copolymer P(VP-co-VAc)3070 containing the least VP fraction in the three copolymers, its blends with OSL exhibited a single T_g varying systematically with OSL content. Therefore, it can be safely concluded that the use of P(VP-co-VAc) containing ≥ 30 mol % VP residues results in a good miscibility state of the blends with OSL.

OSL(-Ac)/VP-containing vinyl polymer complex

As an extension of the miscibility of OSL blends with PVP, further insight was provided into the

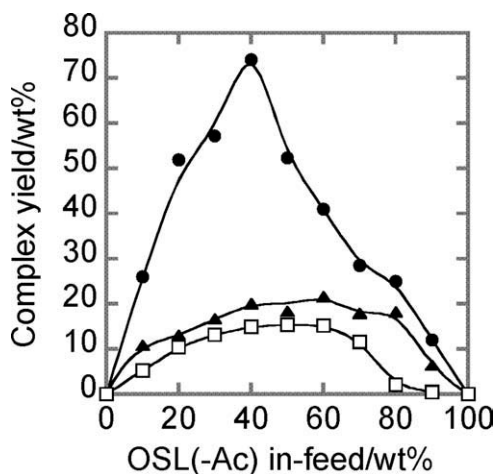


Figure 6 Plots of the yield of complex-like precipitate versus blend composition [weight percentage of OSL(-Ac) in feed] for mixtures of OSL(-Ac) and PVP solutions. Degree of acetylation: ●, 0%; ▲, 60%; □, 100%.

intermolecular interaction between the two polymer components. The mixing of two polymer solutions, OSL(-Ac) in THF and a VP-containing vinyl polymer in the same solvent, led to immediate occurrence of a brown precipitation. This is not the case of usual segregation of different polymers. When an exothermic interaction stronger than the respective polymer-solvent interactions acts between the pair polymers, an insoluble complex-like agglomerate may be formed in the precipitation. Actually, PVP is known to form interpolymer complexes with polymers containing strong proton-donating groups such as poly(acrylic acid) and poly(methacrylic acid),²⁸ aliphatic hydroxyl-containing polymers [e.g., poly(2-hydroxypropyl methacrylate) and poly(styrene-co-allyl alcohol)²⁹], cellulose acetate,³⁰ and phenolic polymers (*p*-bromo-phenol-formaldehyde resin³¹ and *p*-hydroxybenzoic acid-formaldehyde copolymer³²).

The yield of the brown precipitate thus obtained varied according to the in-feed polymer composition in the mixed solution. Data of the yield, defined as weight percentage of precipitate relative to the total weight of polymers existent in the respective mixed solutions, are presented in Figure 6 for three series of OSL(-Ac)/PVP complexes. As can readily be seen from the figure, the yield of complex depends on the in-feed polymer composition, and the maximal yield is observed when the OSL(-Ac) proportion of mixing is roughly 40–60 wt %. It is also found in Figure 6 that the higher the degree of acetylation of the OSL used, the more greatly the yield of complex decreases in the entire range of in-feed composition, implying depression in the capability of OSL to form the complex with a diminish in the number of the hydroxyl groups. In addition, the OSL(-Ac) proportion in-feed with the highest of the complex yield increased with an increase in the acetylation degree, which can be attributed to the decrement of hydroxyl groups in OSL by acetylation.

Elemental analysis was carried out for the OSL/PVP complexes to estimate their actual composition. The results are summarized in Table II. It is found from the data that the polymer composition in the

TABLE II
Data of Polymer Composition for OSL/PVP Mixtures
Precipitated from THF Solutions

OSL/PVP in feed weight ratio	Composition in precipitate (wt/wt)
20/80	19/81
40/60	29/71
60/40	36/64
80/20	43/57

complex-like products depends on the in-feed composition, but there is less stoichiometric relationship in the coprecipitation, suggesting almost no incidence of such a regularly assembled structure as that in a ladder-type polymer complex.³³ Furthermore, there arises a difference regarding the extent of compositional discrepancy between the precipitated OSL complexes with PVP, that is, the composition is richer in the VP component when compared with the corresponding composition in feed. Thus, it is likely that a larger number of the interactive sites in the vinyl polymer component leads to the precipitation with a smaller quantity of the OSL ingredient. This may be a consequence of easier attainment of the intermolecular interactions in excess of a limiting frequency required for forming an insoluble polymer complex.

Figure 7 shows the yield data observed for other series of OSL/vinyl copolymer complexes, again plotted against in-feed OSL proportion in the mixed solutions, in which the VP/VAc ratio in the copolymer is a changing factor. When the VP fraction in the vinyl polymer component is lowered, the complex yield also decreased, indicating that the VP side group participates in the OSL/vinyl copolymer complexation.

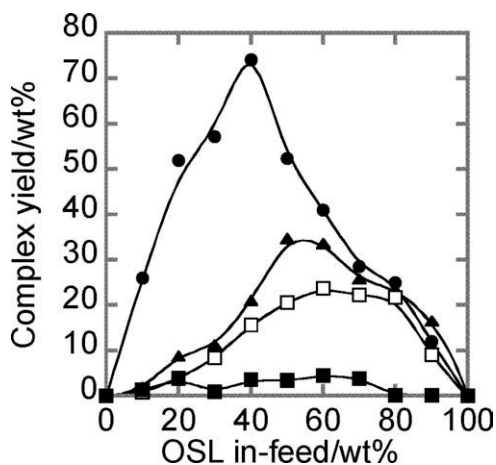


Figure 7 Plots of the yield of complex-like precipitate versus blend composition (weight percentage of OSL in feed) for mixtures of OSL and P(VP-co-VAc) solutions. VP/VAc ratio in P(VP-co-VAc): ●, 100/0; ▲, 70/30; □, 50/50; ■, 30/70.

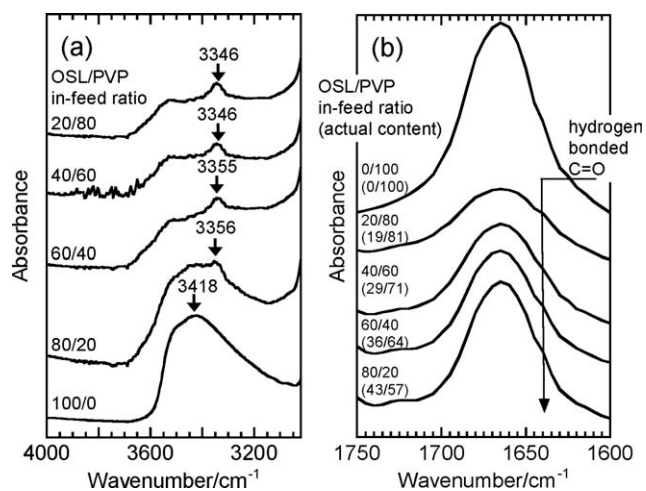


Figure 8 FTIR spectra of OSL, PVP, and their complexes in the frequency regions of (a) O—H and (b) C=O stretching vibrations.

FTIR spectra (Fig. 8) for the OSL/PVP complexes exhibited both the prominence at $\sim 3350 \text{ cm}^{-1}$ (O—H of OSL) and shoulder at $\sim 1635 \text{ cm}^{-1}$ (C=O of PVP), displaying the development of hydrogen bonding. Thus, it can be reasonably assumed from these results that the complex attendance on mixing is dominated substantially by the number of hydroxyl groups of OSL(-Ac) and carbonyl groups of the VP fraction. In addition, as the complex formation was observed even for OSL-Ac100/PVP as shown in Figure 6, there may collaterally exist other interactions as has been pointed out above for the interpretation of the blend miscibility of this combination.

In Figure 3, T_g data for the OSL/PVP complexes are plotted as a function of OSL fraction and compared with those obtained for the corresponding blends. Here, the OSL fractions of the complexes are the ones determined by the elemental analysis, and the plot for blends has already been discussed in the above section. As is apparent in this figure, the T_g values of the complexes are always higher than those of OSL/PVP blends having the corresponding compositions and show a large positive deviation from a line according to a simple additive rule of mixture. Such a positive deviation of T_g has been experienced, for instance, in cellulose acetate/PVP mixtures³⁰ and PVP/poly(4-hydroxystyrene) mixtures.³⁴ The present observation indicates that a high frequency of interactions combined OSL with PVP intimately in the complexes to seriously reduce the mobilities of the individual polymer chains.

CONCLUSION

The miscibility characterization was performed on binary blends of OSL with synthetic homopolymers and copolymers containing a VAc and/or VP unit.

From the measurements of thermal transition behavior by DSC, it was found that OSL/PVAc blends are immiscible, whereas PVP forms a miscible monophase with OSL and OSL-Ac irrespective of the degree of acetylation. Concerning the vinyl copolymers of VP and VAc, they are miscible with OSL when the VP fraction in P(VP-co-VAc) is ≥ 30 mol %.

FTIR measurements revealed the presence of hydrogen bonding interactions between hydroxyls of OSL and carbonyls of VP in the miscible blends of OSL/PVP. The mixing state in this system appears to depend primarily on whether or not a given pair can produce an effective number of attractive hydrogen bonding interactions. However, hydrogen bonding was not applicable for the miscibility attainment for the fully acetylated OSL (OSL-Ac100), which was supported by the spectroscopic measurements. Further characterization will be required to clarify the existence of the driving force for the miscibility achievement other than hydrogen bonding.

On the other hand, by simply mixing OSL(-Ac) and VP-containing polymer solutions in a solvent THF, both polymer components precipitated spontaneously to form complex-like agglomerate because of stronger attraction in preference to their respective solvations; however, the product was accompanied by less stoichiometric structure. The yield of precipitate diminished with increasing the degree of acetylation of OSL and with decreasing VP fraction in P(VP-co-VAc).

These findings are expected to be useful for improvements in film formability and other physical properties of OSL. Even though PVP provide a miscible system with OSL, bulk materials of the resultant miscible blend are too brittle. Such a drawback would be avoided by means of blending with the copolymer P(VP-co-VAc). From a functional viewpoint, the water absorption property of the blend system would be widely variable by altering the binary polymer composition and the ratio of hydrophilic/hydrophobic (VP/VAc) residues in the copolymer. This may be of significance in the applications to medical and sanitary areas. Another significant topic is the utilization of PVP as a compatibilizer for lignin-containing ternary systems. A possible approach is the formation of intimate mixing of lignin with cellulose acetate, which is known to be miscible with PVP.³⁵ Study on such a ternary composite system is in progress and will be reported somewhere in no distant future.

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