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Molecular complex of lignosulfonic acid/poly(vinyl pyridine) via ionic interaction: characterization of chemical composition and application to material surface modifications

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Abstract Poly ion complexes of anionic lignosulfonic acid (LSA) with cationic poly(2-vinyl pyridine) or poly(4-vinyl pyridine) were prepared by mixing the polymer solutions in dimethyl sulfoxide or dilute hydrochloric acid. The complexes were formed as soon as the polymer solutions were mixed. Fourier transform infrared (FTIR) measurements for the complexes revealed the presence of strong ionic interactions between sulfonate anions of LSA and pyridinium cations of the vinyl pyridine (VPy) polymers. The strong interaction was supported by detection of a glass transition temperature (T_g) much higher than pristine T_g values of VPy polymers in differential scanning calorimetry. By using the ionic complexation, a coating of LSA onto VPy polymer films was undertaken to modify their original surface property. Formation of a thin complex film was confirmed by observation of absorption bands that are characteristic of the pyridinium cation in reflection FTIR spectra measurements, and by visualization of the attached LSA component in atomic force microscopy. This treatment resulted in the surface of the VPy polymer films becoming hydrophobic. An adhesion test was also conducted by pasting two veneered woods with the polymer complex, followed by shear-tearing them off. The adhesive strength of the complex was estimated to be 1.1 MPa.

Key words Lignosulfonic acid · Poly(vinyl pyridine) · Poly-ion complex · Adhesive

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Introduction

The importance of polymer–polymer blends is now well established as an alternative way of developing completely novel polymers. Furthermore, polymer blending can offer opportunities to modify the thermal and other physical properties of target polymers. Therefore, both practical and fundamental studies have been conducted with a number of polymer pairs. However, it is generally difficult to prepare miscible blends, due to less contribution of the mixing entropy, and, therefore, in most cases, some attractive intermolecular interactions between the component polymers should be adopted to attain the miscibility or good practical compatibility.

As a natural phenolic polymer, lignin, its blends, and other compositions with synthetic polymers have been investigated many times over the past two decades^{1–3} to utilize the woody biomass as useful materials. Recently, a few research groups focused on the intermolecular interactions to obtain lignin-based polymer blends; for example, a hydrogen-bonding attraction^{4–6} and a specific structure of the counterpart polymer^{7,8} were utilized as a driving force to enhance the miscibility or compatibility of two constituent polymers.

From a standpoint of application of polymer chemistry to the field of wood material science, some of the well-established methods to contrive diverse multicomponent polymeric materials based on celluloses^{9–17} may be useful for designing new microcompositions of lignin. Cellulosic polysaccharides and their derivatives can be converted into various morphological types of microcomposites including miscible polymer blends and interpenetrating networks. In the simple case of blending, possible factors to realize the miscibility are ionic interactions,^{18,19} hydrogen bonding,^{14,15,17} dipole–dipole attractions,⁹ and strong affinity in molecular structures.¹⁴

The purpose of the present study was to show an example of useful microcomposites of lignin/synthetic polymer formed via intermolecular interactions. Anionic lignosulfonic acid (LSA) was employed as a lignin sample. LSA is

produced as a by-product in the sulfite pulping process, which is used in several industrial fields, and it is mainly used as a dispersant or binder at present. The counterpart polymers were vinyl pyridine (VPy) homopolymers; in the molecular structure, the nitrogen atom of the pyridine ring side group can act as a proton acceptor. There are two structural isomers in the VPy polymers; that is, poly(2-vinyl pyridine) and poly(4-vinyl pyridine). In the literature, there are several articles reporting polyblends composed of a VPy polymer and another synthetic polymer with a proton-donating moiety.^{20–24}

From a practical point of view, the multicomposition with such a vinyl polymer may improve the processability of LSA, which is not utilized in large quantities because of brittleness due to low molecular weight. Moreover, the VPy polymers used in this study have been suggested to show good compatibility with cellulose.^{25,26} In addition to this compatibility, because LSA is originally derived from protolignin, the LSA/VPy polymer combination may provide beneficial modifications to conventional woody articles. A similar approach can be applied for sulfuric acid lignin as a by-product in the acid saccharification of woody materials to produce sugar feedstock or ethanol by fermentation.^{27,28}

In the present study, different conditions for mixing LSA with poly(vinyl pyridine), involving selection of solvent, type of VPy polymer, and the mixing procedure, were examined to control the degree of ionic interactions and to diversify the range of microcomposites resulting as molecular complex in wood-related industries. Measurements including thermal analysis, infra-red absorption spectroscopy, and atomic force microscopy were performed to clarify the emergence of the intermolecular ionic interaction between LSA and VPy polymers.

Experimental

Materials

A H⁺ form of LSA was prepared by ion exchange with Na⁺ of lignosulfonic acid sodium salt (LSA-Na) (Aldrich). The nominal molecular weight of LSA-Na was 5000. First, 60 g of LSA-Na was dissolved in 1000 ml of distilled water and 150 g of ion-exchange resin [Amberlite IR-120 PLUS (H), MP Biomedicals] was added to the LSA-Na aqueous solution. The mixture was stirred at 20°C. After 2 h, the ion-exchange resin was separated by filtration. The LSA thus obtained in aqueous solution as the H⁺ form was concentrated and then freeze-dried for 24 h.

The vinyl polymers used as mixing partners of LSA were poly(2-vinyl pyridine) (P2VPy) and poly(4-vinyl pyridine) (P4VPy). These two VPy polymer samples were purchased from Scientific Polymer Products; their nominal weight-average molecular weights were 150 000 (P2VPy) and 160 000 (P4VPy). Dimethyl sulfoxide (DMSO) and 1 M hydrochloric acid were obtained from Nacalai Tesque. Chemical structures of the lignosulfonic acid and VPy polymers are shown in Figure 1.

Quantification of functional groups of LSA

The contents of functional groups (hydroxyl, methoxy, and sulfonate groups) were determined according to literature methods,²⁹ but with adequate modifications. LSA was acetylated and then hydrolyzed to determine the content of hydroxyl groups.^{30–32} The concentration of free acetic acid released due to the hydrolysis was determined with a Shimadzu LC-10A liquid chromatography apparatus equipped with refractive index detector RID-10A and a Shimpack SCR 102H (8.0 × 300 mm) column using 0.024% (w/w) HClO₄ aqueous solution as an eluent.

The content of methoxy groups was determined by a literature method.^{33–35} Hydroiodic acid (12 ml) and 25 mg of red phosphorus were stirred and refluxed at 145°C under nitrogen atmosphere for 2 h. LSA (54.5 mg) was added into the mixture and stirring was continued for 1 h. The refluxed gas was washed with saturated sodium bicarbonate solution and then absorbed into 100 g of 96% acetic acid aqueous solution/sodium acetate (80/20 in weight) containing 5 g of bromine. After absorbing the gas, 7.5 g of sodium acetate was added into the solution, and then formic acid was added to the combined reaction mixture until the brown color of the bromine disappeared completely. Sulfuric acid solution (10% w/w, 15 ml) and 6 g of potassium iodide were added to the resulting solution. After standing for 5 min, the solution was titrated with 0.05 N sodium thiosulfate until the color of the liberated iodine nearly disappeared. Starch solution (1%, 1 ml) was added and the mixture was further titrated until the iodine-starch blue color was completely removed according to the naked eye.

The content of sulfonate groups was determined by electro conductivity titration. LSA (0.99 g) was dissolved in 150 ml of 0.001 M sodium chloride solution. A 50-ml aliquot of this solution was titrated with sodium hydroxide (0.1 M) by means of a conductometric method with a Kyoto Electronics AT-510 titration cell. The sulfur weight fraction in LSA was also determined by elemental analysis at the

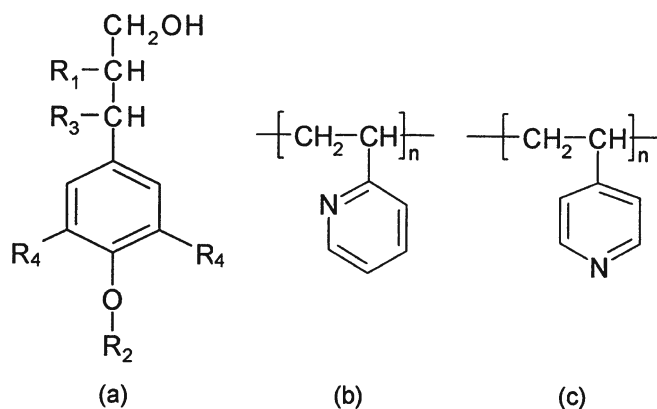


Fig. 1. Chemical structures of **a** typical phenyl propane unit of lignosulfonic acid (LSA) (R_1 and R_2 = H or lignin; R_3 = H, OH, or SO_3H ; R_4 = H or OCH_3), **b** poly(2-vinyl pyridine) (P2VPy), and **c** poly(4-vinyl pyridine) (P4VPy)

Center for Organic Elemental Microanalysis in Kyoto University, and the content of the sulfonate groups was calculated from the value. The phenyl propane unit formulae of the LSA used could be determined to be $C_9H_{11.07}O_{3.55}S_{0.56}(OH)_{1.69}(OCH_3)_{0.20}$.

Preparation of complex samples via mixing of LSA and VPy polymer solutions

Complex samples were prepared by mixing LSA and VPy polymer solutions. LSA and VPy polymer dried at 40°C in vacuo for 24 h were dissolved separately in DMSO and stirred for 1 day. The concentration of each solution was 1% (w/w). The paired polymer solutions were mixed with each other in the desired proportions to give a dark brown precipitate that formed spontaneously. After stirring for 24 h at 25°C, each suspension was centrifuged at 10000 rpm for 5 min and washed with diethyl ether. The purification procedure involving centrifugation and washing was repeated three times. The precipitates thus obtained were then dried at 40°C in vacuo for 24 h. On the other hand, LSA and VPy polymer control samples were prepared in powder and film form, respectively, from their solutions by solvent evaporation. After stirring for 1 day at 25°C, each solution was poured into a Teflon tray and the control samples were obtained by solvent evaporation at 50°C under reduced pressure (<10 mmHg) for 3 h or longer if necessary. After the evaporation, the control samples were washed with diethyl ether and then dried at 40°C in vacuo for 24 h. Complex samples were also prepared from polymer solutions in dilute hydrochloric acid (pH 1 or 3), in the same manner as that mentioned above. In order to prepare LSA and VPy polymer control samples in these solution systems, the rotary evaporator was operated at 60°C for 1% (w/w) solutions. After evaporation, the control samples were obtained by freeze drying. Before commencing differential scanning calorimetry (DSC) measurements, the prepared samples were further dried at 40°C in vacuo for 1 day.

Complex preparation on VPy polymer films: hydrophobization of VPy polymers

Glass slides (76 × 26 mm) coated with a 30-nm gold layer with a Jeol Fine Coat JFC-1100E ion sputter were used as substrate. The glass slides were dipped in a 2% (w/w) VPy polymer solution in ethanol. After air drying the slides, films of VPy polymers were obtained. To smooth the surfaces of the polymer films, they were heat-treated in an oven at 120°C (for P2VPy) or 180°C (for P4VPy) for 5 min. These films were then dipped in an aqueous solution of LSA (0.01%, 0.1%, or 1.0% w/w) at 25°C and drawn out after 30 min, followed by washing with distilled water for 10 s. The LSA-coated films were dried at 50°C in vacuo for 24 h.

Measurements

Fourier transform infrared (FTIR) spectra were recorded with a Shimadzu FTIR-8600PC spectrometer with a resolution of 4 cm⁻¹. A standard KBr-pellet method was used to examine the type and degree of intermolecular interaction of the complex samples prepared by solution mixing. FTIR reflection absorption spectroscopy (FTIR-RAS) was applied to detect a scarious complex formed on VPy films. A Shimadzu RAS-8000 reflection attachment was used at an incident-beam angle of 70°, together with a Shimadzu GPR-8000 wire grid polarizer.

DSC was carried out on ca. 5-mg samples with a Seiko DSC6200/EXSTAR6000. The measurements were performed at a rate of 20°C/min under a nitrogen atmosphere after calibration of the temperature readings with an indium standard. The samples were first heated up to 220°C (P2VPy and P4VPy homopolymers), 250°C (LSA/P4VPy complexes), or 300°C (plain LSA and LSA/P2VPy), and then immediately quenched to -100°C with liquid nitrogen. The second heating scans were run from -100°C to 220°C (P2VPy and P4VPy homopolymers), to 250°C (LSA/P4VPy complexes), or to 300°C (plain LSA and LSA/P2VPy) in order to record stable thermograms. Their glass transition temperatures (T_g) were evaluated as the midpoint of a baseline shift appearing in the respective DSC thermograms. Elemental analysis was carried out with a Yanaco CHN Corder MT-3 at the Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Sciences, Kyoto University.

Contact-angle measurements were made with a Kyowa Interface Science Drop Master 500 to evaluate the hydrophobicity of the surfaces of the VPy films dipped into LSA solutions. Distilled water (3.0 μl) was dropped on the respective films and the contact angles of water were measured after 0.5 s. The measurements were repeated ten times for plain VPy polymer films and five times for the polymer films coated with LSA.

Surface morphology of the VPy polymer films dipped into LSA solutions was examined by atomic force microscopy (AFM) with an Olympus NV2000 apparatus. A noncontact mode was utilized with a low-resonance-frequency-type Si tip of 20-nm radius (Olympus AC240TS-C1). The scanning size was 30 × 30 μm.

Adhesive measurements were conducted at 20°C with specimens of two mutually pasted veneered lauan three-ply boards (85 × 25 × 10 mm). The area of adhesion was 13 × 25 mm. A 1% (w/w) LSA aqueous solution and a 5% (w/w) VPy aqueous polymer solution, both adjusted to pH ~ 1, were pasted on the respective veneered wood boards. The applied quantities of the respective solutions were both fixed at 1 ml. Subsequently, these two boards were compressed at 1.5 MPa and allowed to stand for 24 h. Tensile behavior was examined using a Shimadzu Autograph AGS-5kNG. The tensile stress was applied parallel to fiber direction of the surface layers. The strain rate and span length were 0.5 mm/min and 40 mm, respectively. Five specimens of a given polymer pair were employed to estimate the average adhesive tensile strength.

Results and discussion

Aggregated complex formation via mixing of LSA and VPy polymer solutions

The mixing of LSA and VPy polymer solutions led to immediate occurrence of brown precipitates. Since an exothermic interaction stronger than the respective polymer–solvent interaction occurred between the paired polymers, an insoluble complex agglomerate formed to produce a precipitate. In the present study, the driving force to form the complex precipitate may be considered as the ionic interaction between sulfonic anions of LSA and pyridinium cations of VPy polymers, as discussed below.

FTIR spectroscopy

One of the powerful tools to investigate the intermolecular interactions in polymer blends and composites is FTIR spectroscopy. Figure 2 shows the FTIR spectra of LSA, P2VPy, and P4VPy homopolymers, and the LSA/VPy polymer complexes formed via mixing their DMSO solutions. The samples designated as 0/100 and 100/0 are VPy polymers and LSA cast from DMSO, respectively. There was no difference between as-supplied VPy polymers and the as-cast VPy polymers (0/100) from DMSO solution. Stronger peaks at 1590 cm^{-1} (P2VPy) and 1597 cm^{-1} (P4VPy) are associated with a major ring-stretching mode for the 2- and 4-substituted pyridine groups, respectively.^{36–38} Also, the secondary peaks at 1570 cm^{-1} (P2VPy) and 1558 cm^{-1} (P4VPy) can be assigned to the ring-stretching vibration of the pyridine groups. The other phenolic polymer LSA has a broad band at 1597 cm^{-1} , which can be assigned to a ring vibration of the benzene unit. The complexes of LSA/P2VPy exhibit major three bands at 1622, 1590, and 1570 cm^{-1} , while the LSA/P4VPy series show similar bands at 1636, 1597, and 1558 cm^{-1} . By comparison between the

spectra of each complex and those of the original polymers, the isolated bands at 1590 and 1570 cm^{-1} (P2VPy) and 1597 and 1558 cm^{-1} (P4VPy) are judged to arise from the VPy polymer components. However, the band appearing at 1622 cm^{-1} (LSA/P2VPy) and that at 1636 cm^{-1} (LSA/P4VPy) have no counterpart in either VPy polymers or LSA per se. Therefore, the emergence of these new bands should be ascribed to the proton transfer from sulfonic groups to pyridine groups on mixing of the two different polymers; viz, these bands are assigned to a ring vibration of pyridinium cations involved in formation of a kind of salt complex. However, the pyridinium bands demonstrate a different behavior from each other. The main difference is the appearance of the peak at 1622 cm^{-1} for P2VPy, whereas in P4VP the 1622-cm^{-1} peak is hardly observable. Although a similar difference has been described previously,³⁹ a straightforward explanation for this difference is not known to us.

Figure 3 shows the FTIR spectra of LSA, P2VPy, and P4VPy homopolymers, and LSA/VPy polymer complexes formed by mixing the respective solutions in dilute acid (pH 1). The samples designated as 0/100 and 100/0 are VPy polymers and LSA, respectively, each cast from the acid solution adjusted at pH 1. All the data are shown on an enlarged scale in the range $1700\text{--}1500\text{ cm}^{-1}$. The two 0/100 samples exhibited no peak at 1570 cm^{-1} (P2VPy) or 1558 cm^{-1} (P4VPy); instead, they gave new bands at ca. 1622 cm^{-1} (P2VPy) or 1636 cm^{-1} (P4VPy). The appearance of these new bands may be attributed to excessive proton transfer from dilute acid (pH 1) to pyridine groups, where it should be noted that the possible salting is as a water-soluble chloride. On the other hand, the complexes also exhibited bands at 1622 cm^{-1} (LSA/P2VPy) or 1636 cm^{-1} (LSA/P4VPy), which are similar to the preceding case with a preparation method of mixing DMSO solutions. In Fig. 3b, however, the band at 1558 cm^{-1} (LSA/P4VPy) is not present, unlike the situation in Fig. 2b. The chlorine contents in the 0/100 samples were evaluated as 21.7% (P2VPy) and 23.0% (P4VPy) by elemental analysis, suggesting that

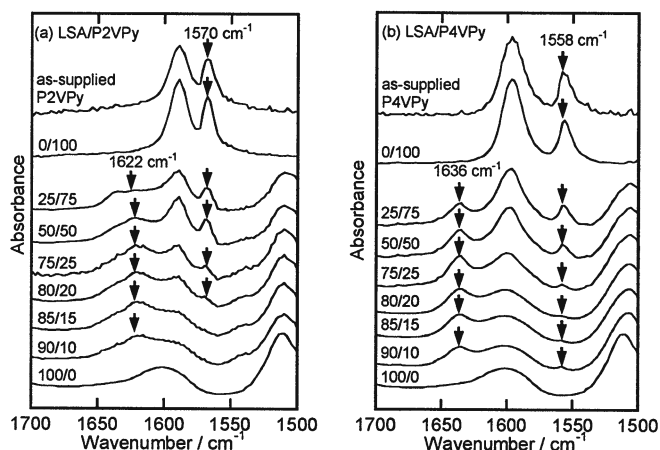


Fig. 2a, b. Fourier transform infrared (FTIR) spectra of **a** LSA/P2VPy and **b** LSA/P4VPy complexes formed in dimethyl sulfoxide (DMSO) solutions, represented in an enlarged scale for the wavenumber region of $1500\text{--}1700\text{ cm}^{-1}$. Arrows indicate peaks of interest

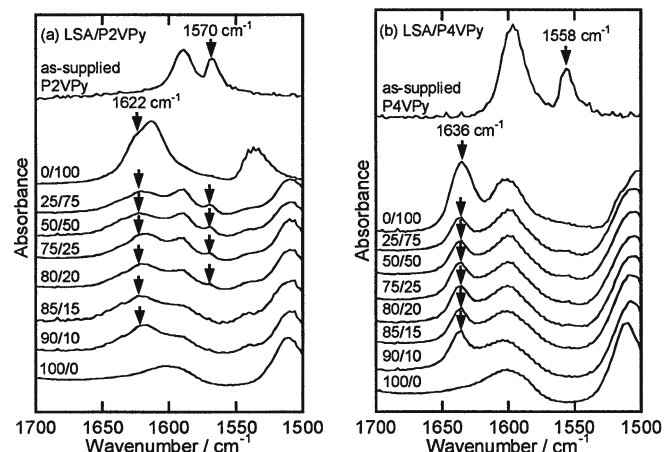


Fig. 3a, b. FTIR spectra of **a** LSA/P2VPy and **b** LSA/P4VPy complexes formed in aqueous solutions (pH 1), represented in an enlarged scale for the wavenumber region of $1500\text{--}1700\text{ cm}^{-1}$

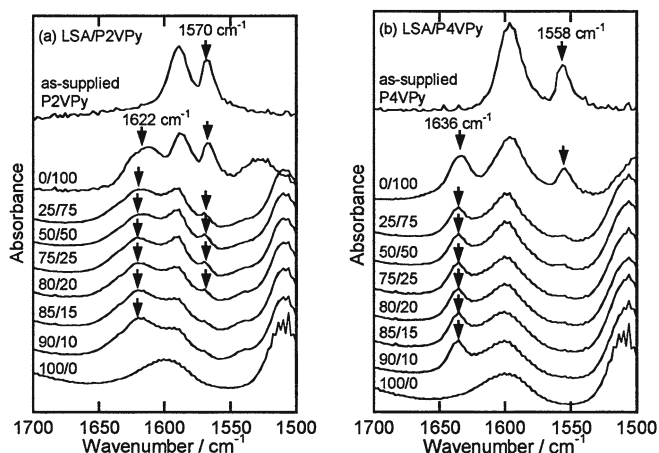


Fig. 4a, b. FTIR spectra of **a** LSA/P2VPy and **b** LSA/P4VPy complexes formed in aqueous solutions (pH 3), represented in an enlarged scale for the wavenumber region of 1500–1700 cm⁻¹

almost all pyridinium cations in the VPy polymers interacted with chloride ion. In contrast, the complex samples were found to contain no chlorine in the elemental analysis. Therefore, it can be reasonably assumed for the complexes that almost all pyridinium cations in the VPy polymers interacted with sulfonate anion of the LSA component, which is consistent with the disappearance or strong suppression of the bands at 1558 cm⁻¹ (LSA/P4VPy) and 1570 cm⁻¹ (LSA/P2VPy).

Figure 4 shows FTIR spectra of LSA, P2VPy, and P4VPy homopolymers, and LSA/VPy polymer complexes formed by mixing their solutions in more dilute acid (pH 3). Again, LSA/VPy polymer = 0/100 and 100/0 denote VPy polymers and LSA, respectively, each cast from the aqueous solution of pH 3. In both spectra of the 0/100 LSA/VPy polymer, the suppression of the bands at 1570 cm⁻¹ (P2VPy) and 1558 cm⁻¹ (P4VPy) are incomplete, differing from the suppression behavior in the corresponding spectra obtained for the system at pH 1. This means that the transfer of the acid protons to the pyridine groups of the vinyl polymers was incomplete at pH 3. Nevertheless, the LSA/VPy polymer complexes provide essentially the same spectral features as those for the complex samples formed at pH 1, possibly both agglomerate formations coming from a stronger ionic association between the sulfonate group of LSA and the nitrilo group in the pyridine ring of VPy polymers. It was also ascertained that the LSA/VPy complexes prepared from the acid medium of pH 3 contained no chlorine.

Figure 5 illustrates FTIR spectra of mechanical mixtures that were obtained by grinding down LSA and poly(vinyl pyridine) grains in the desired weight proportion in a mortar. Samples designated as 25 + 75 are composed of a grinded powder mixture of 25% (w/w) LSA and 75% (w/w) VPy polymer, and the others are defined similarly. As seen from Fig. 5, the mixed samples of LSA + P2VPy = 25 + 75, 50 + 50, and 75 + 25 and those of LSA + P4VPy = 25 + 75, 50 + 50, 75 + 25, and 90 + 10 exhibited, more or less, the 1622 cm⁻¹ band (LSA + P2VPy) and the 1636 cm⁻¹ band

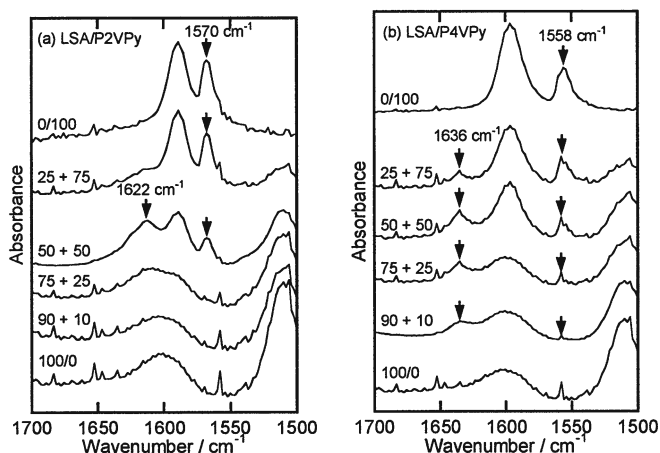


Fig. 5a, b. FTIR spectra of **a** LSA + P2VPy and **b** LSA + P4VPy mixtures mixed in the solid states, represented in an enlarged scale for the wavenumber region of 1500–1700 cm⁻¹

(LSA + P4VPy), respectively. It is thus found that the molecular aggregates of LSA with VPy polymers can be produced by mixing even in the solid state, via the association between the ionizable functional groups of the respective components.

In comparison of the complex-forming behavior between the LSA/P2VPy and LSA/P4VPy series, it may be reasonable to assume that the ionic interaction of P4VPy with LSA is stronger than that of P2VPy. This is because, for any of the preparations using DMSO or aqueous dilute acid as solvent, or simple mechanical grinding, LSA/P4VPy complexes indicated the specific IR absorption band for the pyridinium cation more sharply than the LSA/P2VPy complexes.

DSC measurements

Polymer–polymer miscibility is commonly estimated by determination of the glass transition temperature (T_g) of the blends. If any sample of a binary polymer system exhibits a single glass transition, and a composition-dependent shift in T_g of the blend is clearly observed, then the system can be regarded as highly miscible. Figure 6 compiles DSC thermograms (second heating) of as-supplied and as-cast (from DMSO solution) VPy polymers and LSA/P2VPy and LSA/P4VPy complexes formed via mixing the DMSO solutions. From the midpoint of the discontinuity in heat flow, the T_g values of P2VPy and LSA/P2VPy = 0/100 were 99°C and 101°C (Fig. 6a), respectively. Therefore, the casting process from DMSO solution did not affect the thermal property of the plain P2VPy samples. On the other hand, T_g of LSA cast from DMSO solution (LSA/P2VPy = 100/0) was ill-defined. Concerning the complexes of LSA/P2VPy, a definite signal of the glass transition appeared at a temperature position above 180°C in the thermograms, irrespective of the in-feed composition, as demonstrated in Fig. 6a. Here, attention should be paid to the observation that

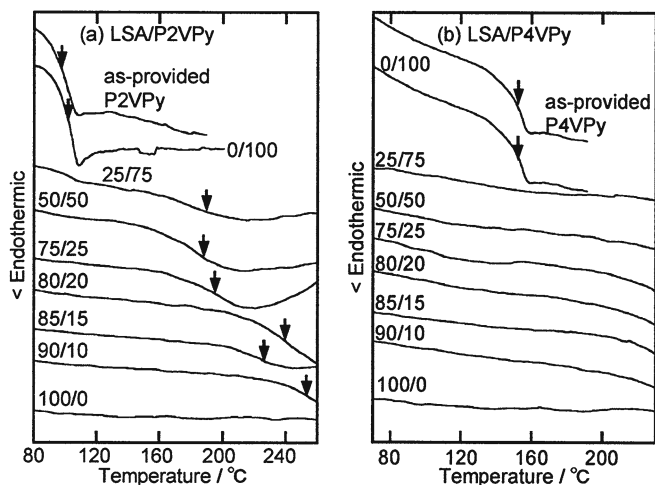


Fig. 6a, b. Differential scanning calorimetry (DSC) thermograms (second heating) of **a** LSA/P2VPy and **b** LSA/P4VPy complexes formed in DMSO. Arrows indicate a T_g position taken as the midpoint of the discontinuity in heat flow

the T_g values of the complexes are always higher than that of the unmixed P2VPy. Furthermore, the absence of multiple T_g values suggests that no phase separation prevails in the complexes.

The other series using P4VPy showed more peculiar behavior in thermal transition (see Fig. 6b). T_g values of the two P4VPy samples were very close to each other, determined as 154°C (as-supplied P4VPy) and 155°C (as-cast P4VPy). Somewhat surprisingly, DSC thermograms of the LSA/P4VPy complexes produced no clear signal of glass transition up to 240°C. On visual inspection, the bulk samples of LSA/P4VPy complex indicated no plastic flow, even at temperatures of 240–300°C where thermal degradation noticeably occurred. Thus, the T_g values of the complexes may be latent in a high-temperature region of $\geq 300^\circ\text{C}$, but the molecular decomposition precedes the glass transition.

Figure 7 shows DSC thermograms (second heating) of VPy polymers and LSA/P2VPy and LSA/P4VPy samples obtained via mixing the aqueous solutions (pH 1) of the respective pairing polymers. In contrast to the case from DMSO solutions, the cast films (designated as 0/100) of both plain 2VPy and 4VPy polymers indicated no clear glass transition up to 220°C. It is presumed that their T_g values were above 220°C due to association of the pyridinium cation with chloride anion.^{40,41} Meanwhile, as can be seen in Fig. 7a, the LSA/P2VPy complexes show a clear, single glass transition and the T_g is much higher than that (99°C) of as-supplied P2VPy. In the other complex series of LSA/P4VPy (Fig. 7b), however, no sample exhibited distinct thermal transitions throughout the second scan or softening in the visual and tactile examination, which was also the case for the LSA/P4VPy complexes formed in DMSO.

Figure 8 includes DSC data (second heating) of VPy homopolymers and LSA/VPy polymer complexes prepared from aqueous solutions at pH 3. Generally, their thermal transition behavior was similar to that of the more acidic

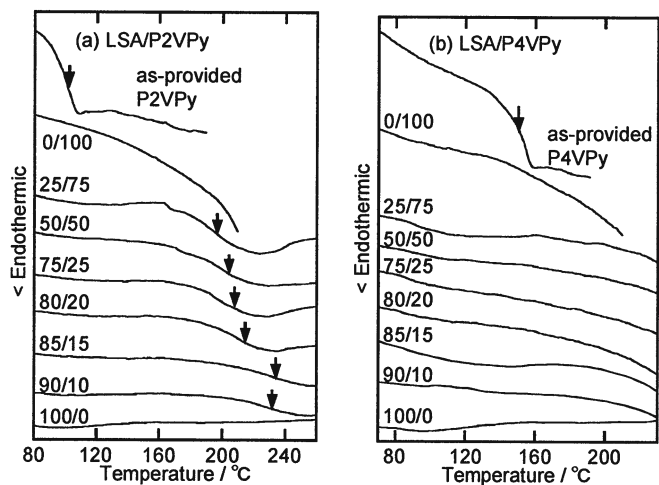


Fig. 7a, b. DSC thermograms (second heating) of **a** LSA/P2VPy and **b** LSA/P4VPy complexes formed in aqueous acid solutions of pH 1

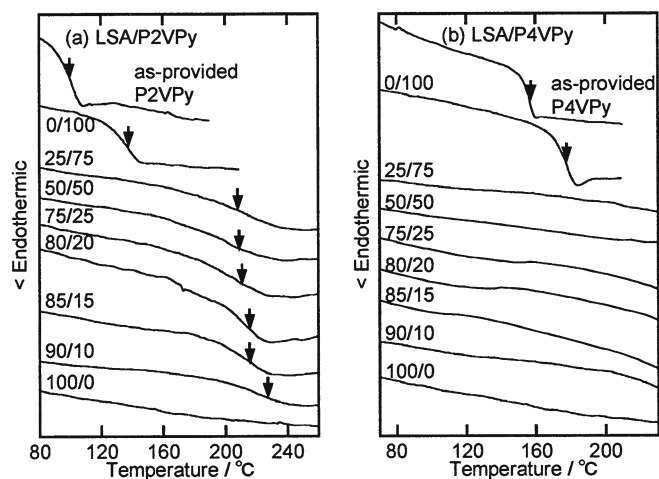


Fig. 8a, b. DSC thermograms (second heating) of **a** LSA/P2VPy and **b** LSA/P4VPy complexes formed in aqueous acid solutions of pH 3

system (pH 1). However, the elevation of the T_g values of the cast VPy polymers (designated as 0/100) was rather moderate, reflecting insufficient coordination of the pyridinium cation with chloride anion, which was also suggested by the FTIR study.

In Fig. 9, T_g data for LSA/P2VPy complexes are plotted as a function of the in-feed molar percentage of the anionic sulfonate group of LSA, defined as $\text{SO}_3^-/[\text{SO}_3^- + \text{NH}^+] \times 100\%$, where NH^+ indicates the pyridinium cation of the VPy polymer component. Although the T_g of LSA was ambiguous, the T_g values of the complexes were higher than that of the original P2VPy. A positive deviation of T_g from a line according to a simple additive rule of mixture has been experienced in some interacting binary systems, for instance, P4VPy/poly(4-hydroxystyrene) mixtures.¹⁸ The present observation suggests that a high frequency of interactions combined LSA with P2VPy intimately in the molecular complex form to seriously reduce the mobility of the

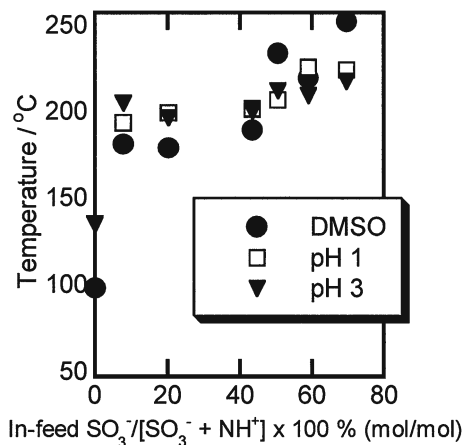


Fig. 9. Plot of T_g versus composition curves of LSA/P2VPy complexes formed with different solvents

individual polymer chains. It should also be noted that the use of different solvents (DMSO and aqueous acid) provided the respective different rates of increase in T_g . This suggests that the degree of interaction in the LSA/P2VPy complex may be controllable by changing the preparation conditions.

The other complex series of LSA/P4VPy showed no glass transition, implying that the ionic interaction, possibly stronger in strength and/or higher in frequency than that formed in the LSA/P2VPy system, strongly suppressed the molecular mobility in the complexes of P4VPy. In fact, the presence of a stronger ionic interaction in the LSA/P4VPy complexes was supported by the FTIR measurements, which revealed a specific pyridinium absorption signal with a sharper and more intense peak, compared with the corresponding signal for the LSA/P2VPy series. In interpretation of the observed difference in the thermal transition between the two complex series, attention should be focused on the difference in positioning of the proton-accepting nitrilo group in the pyridine ring between P2VPy and P4VPy. In P4VPy, the protonated pyridinium assumes a para position, whereas that of P2VPy is ortho. The inferior ionic interaction of the LSA/P2VPy pair, relative to the LSA/P4VPy pair, may be attributed to greater steric hindrance inherent in an ortho-pyridinium substitution of P2VPy, accompanying the association with an LSA sulfonate anion. In contrast, the protonated site in the pyridinium of P4VPy is at maximum distance from the main skeleton of the vinyl polymer and is more favorably located for association with the LSA anionic group.

Yield of agglomerated complexes

The yield of the complex obtained as a dark brown precipitate varied according to the in-feed polymer composition prescribed in the mixing of two solutions. Data of the complex yield, defined as weight percent precipitate relative to the total weight of polymers present in the respective original mixed solutions, are presented in Fig. 10; here, the

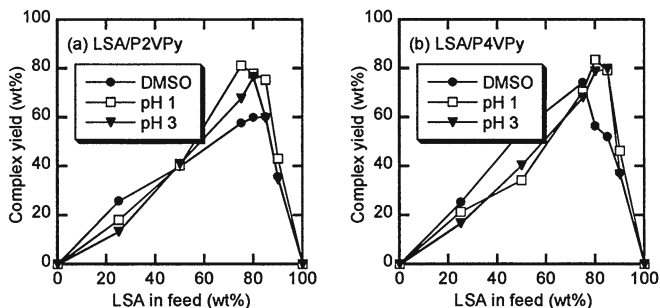


Fig. 10a, b. Complex yields of **a** LSA/P2VPy and **b** LSA/P4VPy formed in DMSO and aqueous solutions (pH 1 and pH 3), plotted against in-feed LSA fraction

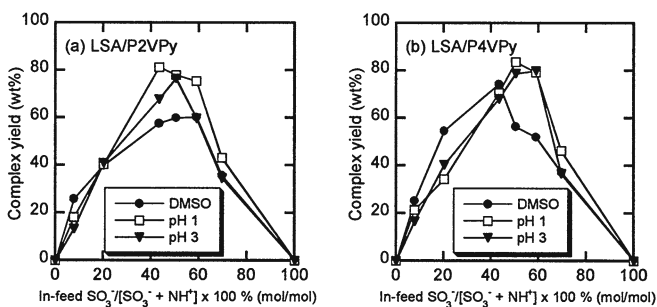


Fig. 11a, b. Complex yields of **a** LSA/P2VPy and **b** LSA/P4VPy formed in DMSO and aqueous solution (pH 1 and pH 3), plotted against in-feed molar percentage of SO_3^-

yield is plotted as a function of the in-feed LSA proportion (% w/w) for the three preparations with different solvents. For all preparations, the complex yield was a maximum when the in-feed LSA proportion was 80% (w/w).

In Fig. 11, the same yield data as above are plotted against the in-feed molar concentration of SO_3^- of LSA, which is defined with respect to the functional groups participating in the complexation. As can readily be seen from the figure, the maximal yield is attained when the in-feed $\text{SO}_3^-/\text{NH}^+$ ratio is approximately 50:50. This result strongly suggests that the complexes are formed stoichiometrically, that is, with equimolar quantities of the complementary functional groups. Elemental analysis revealed that the complexes exhibited to some extent stoichiometrical compositions irrespective of the LSA/VPy polymers feeding ratio. In the preparations with aqueous acids, particularly, it is inferred from the fairly higher yields ($\geq 80\%$ w/w) at the maximum that a considerable amount of sulfonate anions and pyridinium cations are used to form the complexes, although LSA is a three-dimensional polymer molecule. Therefore, the functional sulfonate groups are probably localized on the surface of the LSA molecule in the solutions.

Application of the complex as a novel adhesive for woods

A preliminary experiment was conducted to exploit the present molecular complex as a novel adhesive for woods,

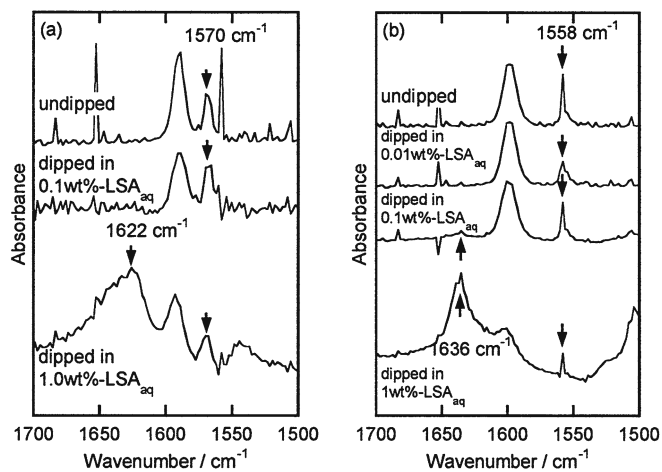


Fig. 12a, b. FTIR reflection absorption spectra of **a** P2VPy and **b** P4VPy films undipped and dipped in a LSA aqueous solution

considering three favorable points: (1) VPy polymers show a high level of compatibility with celluloses,^{25,42} (2) LSA is essentially derived from protolignin in wood, and (3) on mixing the respective polymer solutions, the complex reaction takes place immediately. As a result of the adhesion test, the tensile adhesive strengths for 50/50 LSA/VPy polymer complexes were estimated to be ca. 0.3 MPa (for LSA/P2VPy) and 1.1 MPa (for LSA/P4VPy). On the other hand, the corresponding strength of a commodity-type adhesive of poly(vinyl acetate) emulsion was 3.3 MPa. Therefore, the complex composed of LSA and P4VPy would serve as a glue of relatively stronger adhesive power by further optimizing several parameters including the concentrations of the respective polymer solutions and their molecular weights. As an alternative route, the LSA/VPy polymer complexes may be used as temporary adhesives for moderate applications not requiring particularly high adhesive strengths. Evaluating the water resistance of the adhesives is a significant topic and will be reported in the near future.

Scarious complex formed on VPy polymers

Taking into consideration the ease of forming the ion complexes, we attempted to make a thin coat of the complex on VPy polymer films by dipping the films cast on a glass plate into LSA aqueous solutions of different concentrations. After the dipping treatment, the originally transparent VPy polymer films became slightly brown. Figure 12 illustrates FTIR-RAS spectra of P2VPy and P4VPy films measured before and after the dipping treatment. The spectrum of a P2VPy film dipped in a 1.0% (w/w) LSA solution (Fig. 12a) and those of P4VPy films dipped in 0.1% and 1.0% (w/w) LSA solutions (Fig. 12b) exhibit the specific band derived from pyridinium cation at 1622 cm^{-1} and 1636 cm^{-1} , respectively. This observation implies that LSA molecules in solution at an adequate concentration ($>0.1\%$ w/w) are able to interact with the solid-state VPy polymers, resulting in the

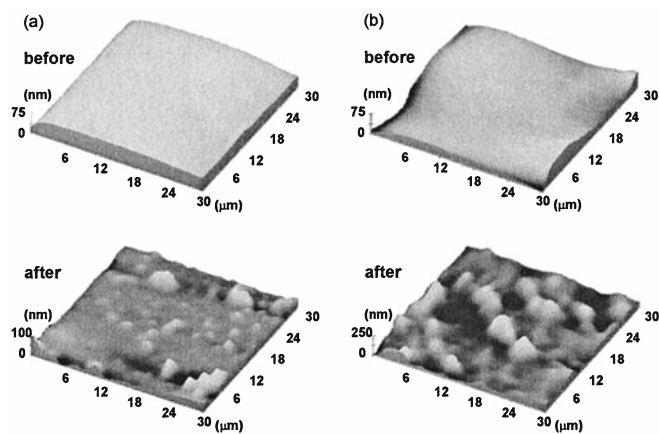


Fig. 13a, b. Atomic force microscopy images of **a** P2VPy and **b** P4VPy films, measured before and after the dipping treatment in a 1.0% (w/w) LSA aqueous solution

formation of the ion complex, possibly at and through the interface between the two phases.

The contact angle of water on the surface of the P4VP film cast on a glass slide was evaluated before and after the dipping treatment as 63.9° for the untreated sample and 76.4° for the one treated in a 1.0% (w/w) LSA aqueous solution. This indicates that the hydrophobicity of the P4VPy film increased. For P2VPy films, however, we could not see such an appreciable difference between before and after the same treatment; the water contact angle was around 66° in each case. This suggests that the density of LSA coated on the surface of the P2VPy film was very low.

Figure 13 displays AFM images of the P2VPy and P4VPy films coated with LSA by the dipping treatment with a 1.0% (w/w) LSA solution. As can be seen from the comparison between before and after dipping in both figures, the treatment develops scarious sediments on the originally smooth surfaces of the VPy polymer films. This observation suggests formation of the complex in a scarious agglomerate via interaction between solute LSA and solid VPy polymer. The respective scarious sediments occupied a circle area with a diameter less than $10\ \mu\text{m}$ on the VPy polymer films. The height of the sediments was less than 100 nm. Taking into account their dimensions, the sediments can be regarded as an assembly containing an appreciable number of LSA molecules. Regarding the extent of development of the scarious sediments, it was apparently greater on the P4VPy film (Fig. 13b) than on the P2VPy film (Fig. 13a). This observation also supports the conclusion that P4VPy complexes with LSA much more strongly than P2VPy.

Conclusions

In the present study, we prepared new examples of lignin-based microcomposites, focusing on intermolecular interactions with different polymers. Simple mixing of LSA and

VPy polymer solutions in DMSO or in aqueous acid provided a complex agglomerate spontaneously, due to the strong intermolecular interactions between sulfonate anions and pyridinium cations. The sharp dependence of the complex yield on the in-feed polymer composition suggested that the complex formation took place stoichiometrically with equimolar quantities of the complementary functional groups. Although LSA is a three-dimensional molecule, the functional groups appear to be localized on the outer surface of the LSA molecule in the solutions. From DSC analysis, it was proved that the LSA/VPy polymer complexes showed markedly high T_g values in comparison with those of the original VPy polymers.

In comparison between the two complex series, LSA/P2VPy and LSA/P4VPy, the interaction of P4VPy with LSA was much stronger than that of P2VPy. FTIR spectra measurements revealed that the LSA/P4VPy complexes gave a much sharper specific absorption band for the pyridinium cation than the LSA/P2VPy series did. Furthermore, the T_g values of the LSA/P4VPy complexes were estimated to be much higher than those of the complexes using P2VPy. The difference in strength of the interaction within the complex for the two complex series was attributed to the difference in positioning of the proton-accepting nitrilo group in the pyridine ring for P2VPy and P4VPy. Taking into consideration the inherent structural factor, the pyridinium cation of P4VPy should be more favorable for the association with the LSA anionic group.

VPy polymer films were coated with LSA by dipping the films in LSA solutions. Thereby the surface of the P4VPy film became hydrophobic; however, the treatment was less effective in the case using P2VPy. AFM observations revealed a scarious sedimentation of the complex on the surfaces of both polymer films, but the extent of the development was greater on the P4VPy surface. This result also supports that the ionic interaction of P4VPy with LSA is stronger than that of P2VPy.

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