

Properties and Structure of PVP–Lignin “Blend Films”

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ABSTRACT: Blend films of poly (4-vinylpyridine) and lignin were prepared by the casting method. Their structure and properties were studied by Fourier transform infrared (FTIR), wide-angle X-ray diffraction (WXR), scanning electron microscopy (SEM), thermogravimetric analysis (TG), and differential scanning calorimetry (DSC). The IR spectra of the blend films indicated that hydrogen-bonding interaction occurred between poly (4-vinylpyridine) and lignin. The glass transition temperature of these blends increased with the increase of lignin content, which indicated that these blends were able to form a miscible phase due to the formation of intermolecular hydrogen bonding between the hydroxyl of lignin and the pyridine ring of poly (4-vi-

nylpyridine). The thermostability of these blends decreased with the increase of lignin content. Initially, an appreciable increase in the measured tensile strength was achieved with a lignin content of 15%, at which the maximum value of 33.03 MPa tensile strength was reached. At a 10% lignin incorporation level, the blend film exhibited a maximum value of 9.03% strain. When the threshold in lignin content for blend films exceeded that limit of 10% lignin, the strain behavior of these blend films deteriorated. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1405–1411, 2005

Key words: hydrogen bonding; poly (4-vinylpyridine); lignin

INTRODUCTION

Polymer blends have been of great interest to materials scientists because they can improve and modify properties over the individual constituent polymers; blending has the effect of toughening and strengthening in engineering applications. Miscibility in polymer blends can be enhanced by specific interaction between the components, such as hydrogen bonding,¹ dipole-dipole, charge transfer, and acid-base complexation. In systems where specific interactions are rather strong, polymers form interpolymer complexes (or simply complexes) as manifested by the formation of insoluble precipitates upon the mixing of two polymer solutions in a common solvent. Polycarboxylic acids, such as poly(acrylic acid) and poly(methacrylic acid), form complexes with poly(4-vinylpyridine)^{2,3} and poly(2-vinylpyridine),^{2,3} and with ternary amide polymers such as poly(*N*-vinyl-2-pyrrolidone)⁴ and poly(2-ethyl-2-oxazoline)^{5,6}. Similarly, polymers containing sulfonic acid groups are also capable of forming complexes with pyridine-containing polymers.^{7–11} In other papers, interpolymer complexation between poly(monoalkyl itaconate) and poly(vinylpyridine) has been reported.^{12–14} Furthermore, interpolymer hydro-

gen bonding and miscibility in poly(vinylpyridine) with phenolic resin and poly(hydroxyether of bisphenol A) have also been studied.^{15–17}

Poly(4-vinylpyridine) (PVP) is a functional polymer that possesses good gas permselectivity.^{18,19} It should be noted that PVP is very brittle and strongly adheres to most solid surfaces, from which it is not possible to remove the membrane easily, to form a free-standing membrane. Lignin is a nontoxic, commercially available, and low-cost natural resource that has the potential to be utilized as a basic raw material in the chemical industry.²⁰ Because of its cementing and protective function in plants, structure, and macromolecular properties, lignin is also an interesting material for use as a component in polymeric blends. Lignin, especially, with its many reactive hydroxyl groups, can form strong hydrogen bonding with many polymers, which would improve and modify the physical properties of the pure polymers.^{21,22} Therefore, a blend film prepared from PVP with lignin could overcome the strong adhesion with most solid surfaces as well as the brittleness of PVP. However, few reports concerning the preparation of PVP/lignin blend film were found.

Based on the information mentioned above, we attempted to introduce lignin into PVP to gain fundamental knowledge in chemistry and physics concerning the hydrogen bonding for lignin and the effects of lignin on the properties.

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EXPERIMENTAL

Materials and preparation of blend films

The 4-vinylpyridine was purchased from Aldrich Chemical Company. PVP was prepared by radical polymerization in mass at 60°C for 18 h under N₂ atmosphere according to the method in reference,²³ with azobisisobutyronitrile (AIBN) (0.5 wt %) as initiator. The resulting product was dissolved in absolute ethanol and precipitated in ether, and filtered and dried under vacuum to produce a white product. Its molecular weight ($M_n = 7.5 \times 10^4$, $[\eta] = 2.5 \times 10^{-3}$ M^{0.68}) was determined by an Ubbelohde viscometer. Alkali lignin from bamboo was supplied by the Guangzhou Chemistry Institute of China.

The PVP and lignin were dissolved in 10 mL DMF to form a 5 wt % solution, and the maximum lignin concentration in the blend was 20%. The polymer solution was poured into a Teflon dish. The solvent was allowed to evaporate slowly from the solution at 30°C for 72 h. The film was dried in vacuum at 90°C for 144 h. By changing the weight ratio of PVP and lignin, from 100 : 0, to 96 : 4, 92 : 8, 90 : 10, 85 : 15, and 80 : 20, in order, a series of blend films, coded as PVP-0, PVP-1, PVP-2, PVP-3, PVP-4, and PVP-5, respectively, were prepared.

Characterization of films

IR spectra of the films in the mode of attenuated total reflection were recorded with a Nicolet (USA) 170SX Fourier transform infrared (FTIR) spectrometer. Film samples, of about 60 μm thickness, were coated with gold in 0.1τ vacuum, then their surface morphologies were observed on a Hitachi S-570 scanning electron micrograph (SEM). The wide-angle X-ray diffraction (WXR) patterns of the films of 60 μm thickness were recorded with a Shimadzu XRD-6000 (Japan) diffractometer by using a Cu K_α target at 40 KV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 50 to 5°.

The T_gs of the film samples, with 1 mm length and 1 mm width, were performed by a Perkin-Elmer Co. (USA) instrument under a nitrogen atmosphere with a flow capacity of 30 mL/min from 20 to 500°C at a heating rate of 25°C/min. A METTLER-TOLEDO DSC822e (CO. Switzerland) was used to measure the glass transition temperature of the PVP/lignin blend films at a heating rate of 10°C/min. All samples were preheated with a scan rate of 20°C/min over a temperature range of 25–170°C and maintained at 170°C for 10 mins to ensure complete removal of the residual solvent. The T_g was taken as the onset point of the heat capacity transition.

The tensile strength (σ_b) and breaking elongation (ϵ_b) of the films were measured on a versatile tensile tester (CMT-6503, Shengzhen SANS Test Machine Co.

Ltd., China) with a tensile rate of 5 mm/min according to the Chinese standard method (GB4456–84). The size of the samples was 70 mm in length, 10 mm in width. There is a distance of 50 mm between two crossheads. The experimental temperature and relative humidity were 20°C and 47%, respectively.

RESULTS AND DISCUSSION

SEM analysis

All the samples prepared were transparent and homogeneous. The color of the samples increased with increasing lignin content, and the color of all the samples except PVP-0 was brown. This observation suggests that the blends are miscible and no phase separation occurs, at least on the scale of wavelengths of visible light. The microscopy of polymer blends could directly reflect on the miscibility. The SEM micrographs of the film's cross-section are shown in Figure 1. As seen from Figure 1, the cross sections of all samples were homogeneous, and displayed in the form of a sandwich, which suggests that these PVP/lignin blends were miscible.

Thermal analysis

The miscibility of a polymer blend can be determined by many techniques, such as thermal analysis, dynamic mechanical analysis, microscopy, and solid state NMR. In general, DSC is the most convenient method to determine the miscibility of polymer blends. Because the structure of lignin is not only chemically complex but also the glass transition phenomenon of lignin is not clearly evident, it is not appropriate to use the "miscibility" or "immiscibility" to describe the blend system. However, if distinct changes of the T_g of the PVP component were observed, the special intermolecular interaction between PVP and lignin would be confirmed. In this study, to detect this parameter, all samples were preheated with a scan rate of 20°C/min over a temperature range of 25–170°C and maintained at 170°C for 10 mins to ensure complete removal of the residual solvent. The DSC curves are shown in Figure 2. It can be seen that the T_g of each blend shifts to higher temperature with the blend composition varying compared with that of pure PVP. The T_gs of all films are 70°C, 82°C, 88°C, 137°C, 139°C, and 147°C, respectively. The T_g of PVP-5 was not clearly evident. The crystallization temperature of the blend films shifts to lower than that of pure PVP-0, and heat enthalpy of crystallization of blend films decreases with an increase of lignin content. This indicates that the degree of crystallization decreases with an increase of lignin content, which is consistent with the data of WXR. Therefore, it can be concluded that PVP/lignin blends are miscible over the

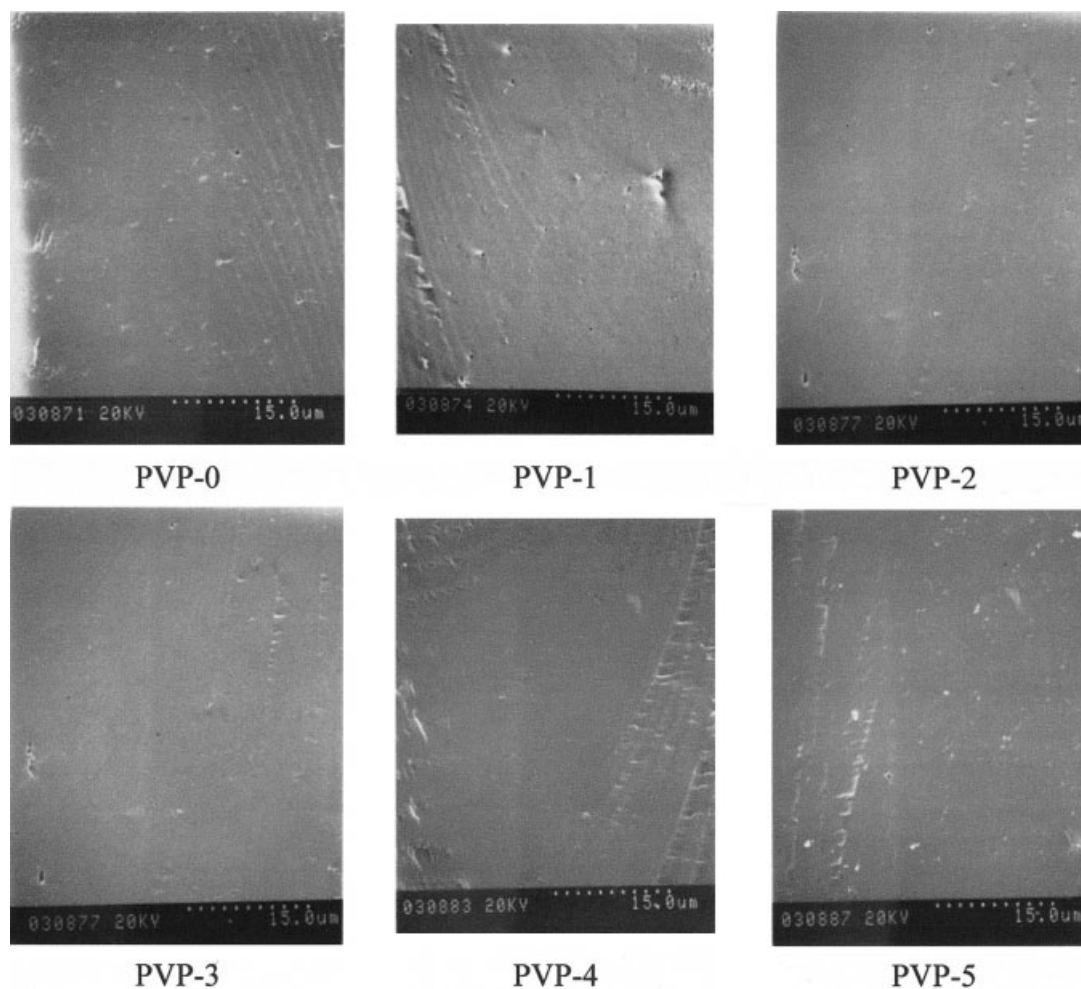


Figure 1 SEM photographs of blend films from PVP and lignin.

entire composition range. This may be caused by the interaction between the hydroxyl groups of lignin and the pyridine groups of PVP; the lignin contains a high density of hydroxyl groups that can interact with PVP through hydrogen bonding. Hydrogen bonding serves as a physical crosslink in PVP and increases its T_g .

TGA is a good method to monitor the process of thermal degradation. The TGA thermograms of the films are shown in Figure 3. All the films show that there is only one step of active weight loss at 25–400°C. The thermal degradation temperatures of the films shift to lower temperatures, which are found at 354°C, 347°C, 337°C, 340°C, 334°C, and 316°C, respectively, and the weight loss rate decreases with increasing content of lignin. The degradation is assigned to the degradation of PVP.²⁴ Because over 354°C the PVP has degraded almost completely, the residue was thought to be almost entirely lignin based. The thermal degradation temperature of the blend films clearly decreases, indicating that lignin has a destabilizing effect on PVP; the existence of lignin in the

blends might aggravate the degradation of PVP at high temperature. It may be that the lignin caused a reduction in the degree of crystallization of PVP, which decreased the thermal stability of the blends. The closest analog of the phenomena is the poly(L-lactic acid)/lignin system.²⁵

X-ray analysis

X-ray diffraction patterns of all samples are shown in Figure 4. Two typical peaks at $2\theta = 10.3^\circ$ and 20.5° were observed for PVP, as reported in reference.²⁶ The X-ray pattern of lignin only shows a typical amorphous peak. If PVP and lignin have low compatibility, each polymer would have its own crystal region in the blend films, and the X-ray patterns of the samples would be expressed as simply mixed patterns of the two polymers with the same ratio as those for blending. However, the patterns of these blend films showed that the peak intensity at $2\theta = 10.3^\circ$ and 20.5° decreased with the increase of lignin content, which implied that the degree of crystallization of PVP decreased. The changes of the patterns indicated

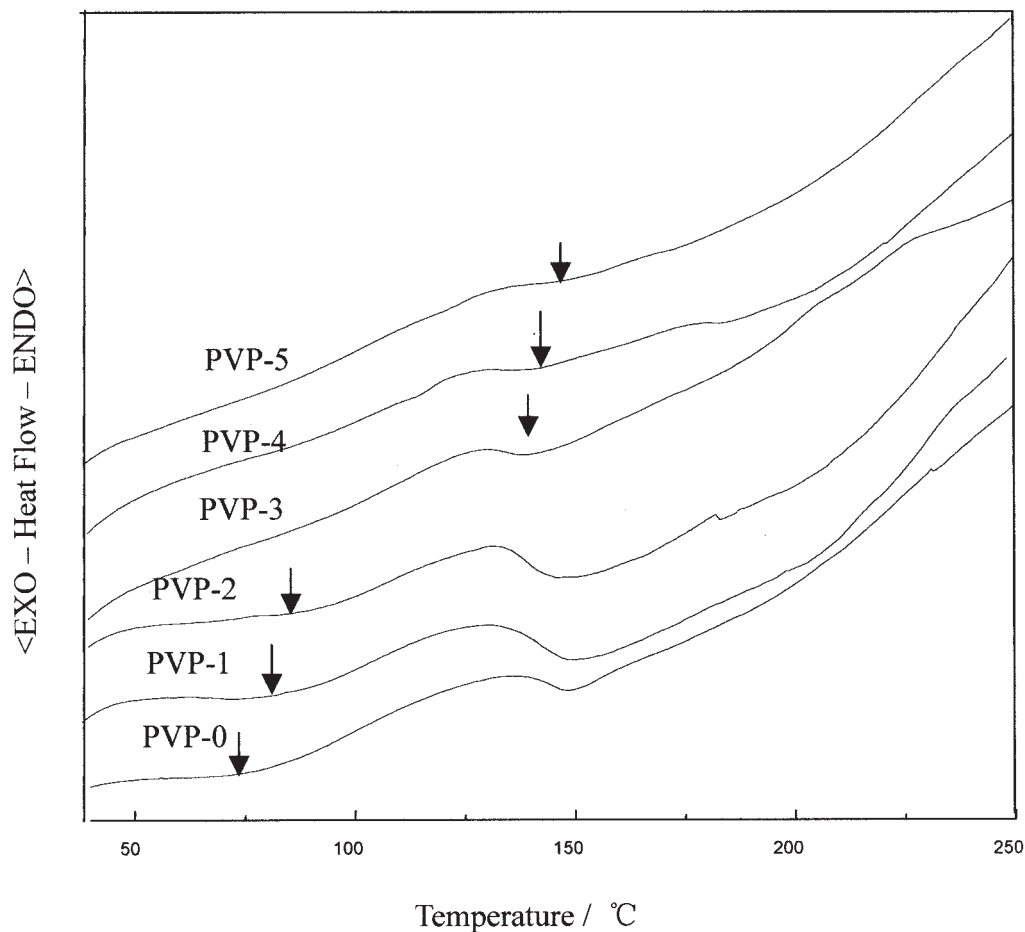


Figure 2 DSC curves of all samples.

that an intermolecular hydrogen bonding interaction occurred between the two polymers, and destroyed the original crystalline domains of PVP. The outcome, deduced from the WXR D, is consistent with that of DSC.

Fourier transition infrared spectroscopy analysis

FTIR spectrometry has been proven to be a very powerful technique to detect the intermolecular interaction between two polymers. The IR hydroxyl stretching

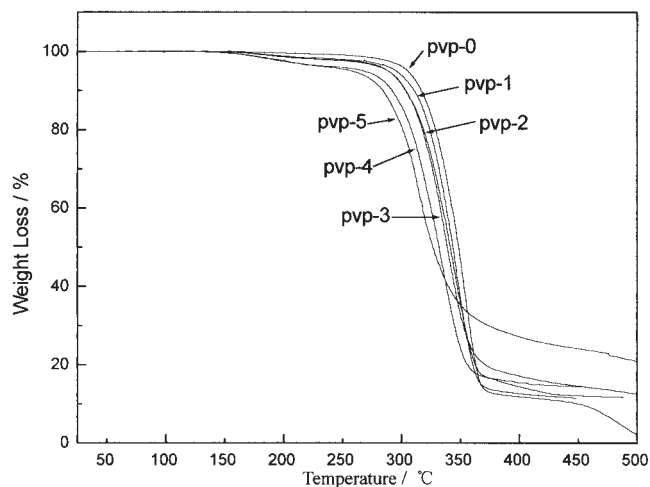


Figure 3 TGA curves of all samples.

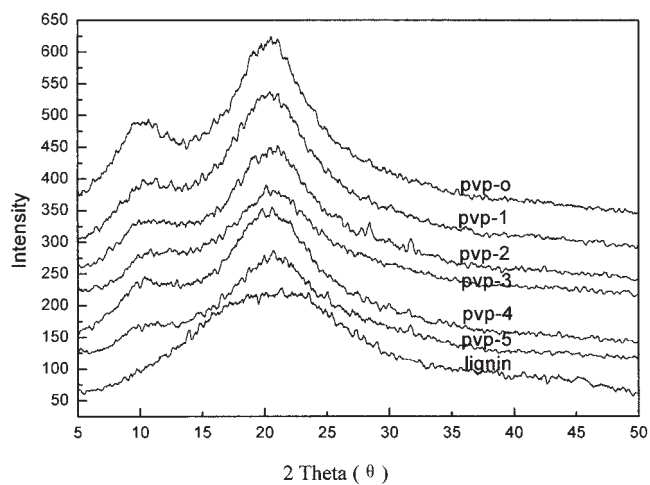


Figure 4 WXR D diffraction patterns of all samples.

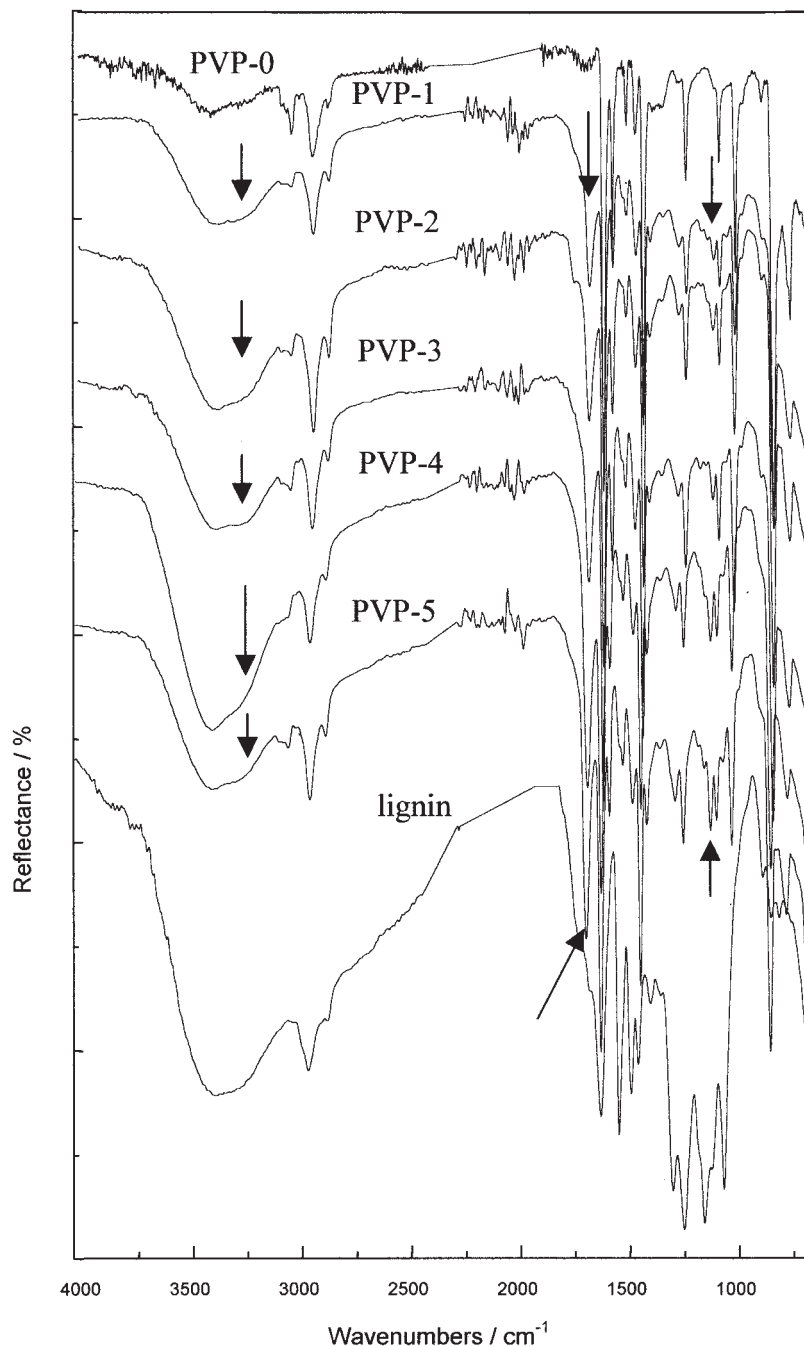


Figure 5 IR spectra of all samples.

range of PVP/lignin blends is sensitive to the hydrogen bonding formation. Figure 5 illustrates the infrared spectra of all samples in the range 4000cm^{-1} – 650cm^{-1} . The molecular structure of PVP reveals that the 1595 , 1557 , and 1495cm^{-1} bands refer to the vibration of $\text{C}=\text{N}$, and $\text{C}=\text{C}$ (pyridine ring),²⁷ and the stretching vibration of the $-\text{CH}=\text{}$ (pyridine ring) is evident at 3124 and 3045cm^{-1} , as shown in curve PVP-0 in Figure 5. As seen in the curve for lignin in Figure 5, the band at 3357cm^{-1} is characteristic of $-\text{OH}$ groups of lignin. The band at 1367cm^{-1} is due to the

bending vibration of the phenolic $-\text{OH}$ group. Bands at 1120 and 1030cm^{-1} are characteristic of the secondary and primary $-\text{OH}$ groups, respectively.²⁸ Moreover, it is clear that a shoulder at 2850cm^{-1} is assignable to vibration of the $-\text{OCH}_3$ groups. Bands at 1456 and 1423cm^{-1} include a considerable contribution from $-\text{CH}$ bands of OCH_3 groups. Two bands at 1595 and 1511cm^{-1} are characteristic of aromatic rings and are due to vibrations of the aromatic skeleton. By comparing the two pure polymers, it is seen that new bands, at 1094 and 1663cm^{-1} , arise in blend films, and the

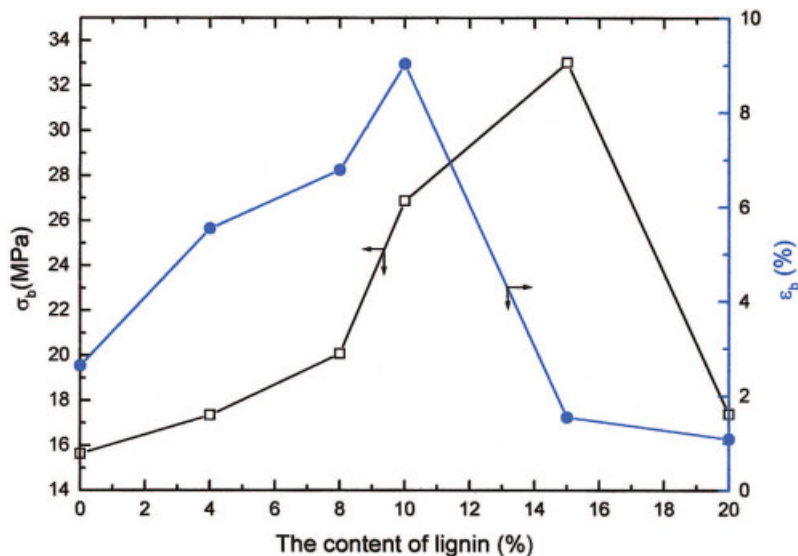


Figure 6 The tensile strength and breaking elongation dependence on lignin content.

intensity of the bands increases gradually with the increase of lignin content. The closest analog of the band at 1663cm^{-1} is the "ammonium" band of the $[-\text{C} = \text{N}^+ - (\text{H}) \text{R}]$ group.^{29,30} The increase of the band intensity suggests that quasi-symmetrical H bonds form between the two polymers.³⁰ The band at 1094cm^{-1} was assigned to the "D-band" of the AH...B complexes.^{15,31} Moreover, the blends show a distinct band in Figure 5, a shoulder at 3221cm^{-1} , from the absorption of the hydrogen-bonded hydroxyl group. It proves that hydrogen bonding was created between PVP and lignin, which created miscibility between PVP and lignin, and improved the physical properties of the blend films.

Mechanical properties

The characterization discussed above indicates miscibility between both molecules in the blends. Tensile properties can provide an answer to this question. The tensile behavior of all samples is shown in Figure 6. The tensile strengths of the blend films change with the increase of lignin content, and the maximum value of 33.03 MPa tensile strength was reached when the content of lignin was 15 wt %. The change of breaking elongation is similar to that of the strength, and the maximum value of 9.03% tensile break elongation was reached when the content of lignin was 10 wt %. The conclusion can be drawn that the lignin introduced to PVP has considerably improved the mechanical properties of the blend films, and the enhancement of tensile strength may be due to hydrogen bonding between PVP and lignin, which gives rise to an intermolecular complex or the physical crosslinkage. The interaction of hydrogen bonding between PVP and

lignin was represented according to references,^{32,33} as shown schematically in Figure 7. So the tensile strength and breaking elongation are higher than those of the pure PVP. When the content of lignin is more than 20 wt %, it may be that micro-domains of lignin existing in bulk gives rise to the poorer tensile strength because lignin does not possess any measurable strength under the testing conditions employed.

CONCLUSIONS

PVP is miscible with lignin due to intermolecular hydrogen bonding between the hydroxyl of lignin and the pyridine ring of PVP over the entire composition range measured. The IR spectra of the blends proved that hydrogen-bonding interaction occurred between PVP and lignin. The glass transition temperature of

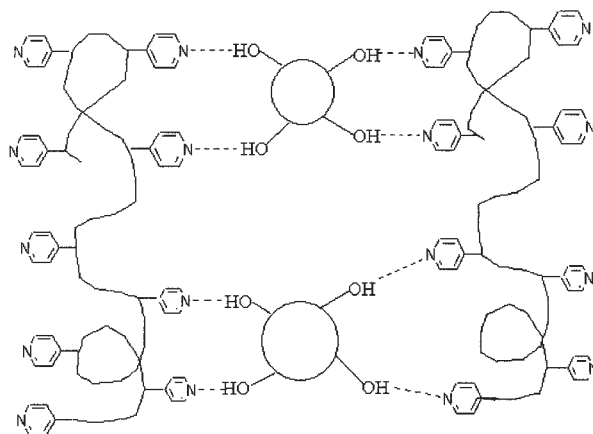


Figure 7 Schematic structure of hydrogen bonding between PVP and lignin.

these blends increased with an increase of lignin content, which indicates that these blends are able to form a miscible phase due to the formation of intermolecular hydrogen bonding between the hydroxyl of lignin and the pyridine ring of PVP. The thermostability of these blends decreases with the increase of lignin content. Initially, an appreciable increase in the measured tensile strength was achieved with a lignin content of 15%, and the maximum value of 33.03 MPa tensile strength was reached. At a 10% lignin incorporation level, the blend exhibited its maximum value of 9.03% strain. When the threshold in lignin content for blends exceeded the range, the tensile behavior of these blends became poorer because of micro-domains of lignin.

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