Quantitative Analysis of Relationship between Hansen Solubility Parameters and Properties of Alkali Lignin/Acrylonitrile–Butadiene–Styrene Blends

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ABSTRACT: Blends of alkali lignin and acrylonitrile–butadiene–styrene (ABS) resin are physically mixed and injected into the injection molding system. Although the components of the blend are bound together by intermolecular forces, noticeable phase separation still occurs. In the present study, inverse gas chromatography technology was used to characterize the Hansen solubility parameters of alkali lignin/ABS blends. The relationship between the Hansen solubility parameters and thermodynamic properties was then determined. Hansen solubility parameters, at room temperature, of alkali lignin/ABS blends containing 0, 10, 20, and 30 wt % alkali lignin were 17.40, 19.20, 18.98, and 17.37 (J/cm$^3$)$^{1/2}$, respectively. Hansen solubility parameters of the blends were shown, both experimentally and theoretically, to be related to their mechanical and thermal properties.

INTRODUCTION

Lignin is an important renewable biomass, second in abundance only to cellulose.$^{1,2}$ Lignin regenerates at a rate of about 150 billion tons per year and approximately 50 million tons of lignin byproducts are obtained from the pulp and paper industries.$^{3,4}$ However, only 1–2% of lignin produced annually is used for the production of value-added products and most lignin is burned for energy.$^{5,6}$ Lignin has a complicated threedimensional reticular structure, incorporating a variety of active functional groups, such as phenol and methoxy groups, which confer advantages including lack of toxicity and degradability.$^{7–9}$ The −OH groups in lignin can form strong intermolecular interactions with other polymers, such as poly(ethylene oxide), poly(4-vinylpyridine), polyaniline, and phenolic resin,$^{10–14}$ and these blends may have improved compatibility and properties. Lignin has also been used to improve the thermal oxidation stability and flame retardancy of polymers, particularly polyethylene and polypropylene.$^{15–18}$ Most polymers are, however, immiscible, with lignin because of low entropy of mixing.$^{10}$ Polymer blends provide a convenient approach for combining the useful properties of two or more polymers and miscibility occurs if the polymers form strong intermolecular interactions, such as hydrogen bonds and acid–base interactions.$^{19}$ Fuller utilization of lignin would significantly benefit the papermaking and biofuel industries.$^{20}$

Acrylonitrile–butadiene–styrene (ABS) resin is an important engineering thermoplastic that is widely used in the manufacture of automobiles, electronic appliances, light industrial appliances and textiles, and in the construction industry, because of its balanced mechanical properties, chemical resistance, ease of processing, and recyclability.$^{21,22}$ ABS composites modified by lignin can improve defects of ABS to achieve target performance and favorable environmental impacts such as flame retardancy and carbon emission reduction and are acceptable for automotive use and other emerging industries such as the automotive side panel.$^{23,24}$ Chains of ABS resin, which contain aromatic structures and strongly polar −CN groups, are similar in structure to lignin, suggesting that the resin may have good interfacial compatibility with lignin. Blending ABS with lignin would make use of lignin and reduce costs, and would concurrently render the ABS nonflammable and partially biodegradable.

Although lignin has been widely used as a raw material to prepare lignin-based blends and composites, these materials had obvious problems with phase separation or incompatibility of the interface.$^{19,25}$ Because the compatibility between two polymers affects the morphology and mechanical properties of the blend or composite, improving the thermodynamic compatibility between the components can prevent coalescence or phase separation during manufacture and use, and thus improve the performance of products.$^{26,27}$ The interface compatibility of blends has typically been studied by characterization from the viewpoint of the chemical structure, by using the change of thermal and mechanical properties to speculate about the mutual relationship between the two components, or by using the swelling method to analyze qualitatively the interaction between the two components.$^{28,29}$ Quantitative characterization of blends of ABS and alkali lignin is, however, lacking and few studies have provided a
quantitative representation of the interactions between the two components and the relationship with their properties.30

The Hansen solubility parameter plays an important role in predicting and improving the compatibility of blends. Inverse gas chromatography (IGC) has been widely used to measure various physical and chemical parameters of polymers, and to determine solubility and interaction parameters.31−34 This technique has proved to be a rapid, direct, and sensitive method for measuring Hansen solubility parameters of polymers and has also been used to measure the compatibility of polymer blends.35−40 In our earlier paper, we had studied quantitatively the polar system of lignin/poly(vinyl alcohol) (PVA) composites.30 To further verify and expand the validity and applicability of the research, the nonpolar system of lignin/ABS blends will be investigated and analyzed. Alkali lignin/ABS blends were injected by the melt blending method and Hansen solubility parameters of the blends were measured by IGC. The correlation between mechanical and thermal properties and Hansen solubility parameters of alkali lignin/ABS blends was then studied quantitively to provide a theoretical basis for the selection and design of technological parameters of ABS/lignin blends.

## RESULTS AND DISCUSSION

### Retention Volumes of Probe Solvents

Special retention volumes were calculated according to the following equation

\[ V_0^s = (t_s - t_r) F \frac{273.15}{mT} \]  

where \( t_s \) and \( t_r \) are the retention time of the probe solvent and the retention of n-pentane, respectively; \( F \), \( m \), and \( T \) are the

| probe solvent | 383 K | 393 K | 403 K | 413 K | 423 K |
|---------------|-------|-------|-------|-------|-------|
| n-hexane      | 0.58  | 0.53  | 0.54  | 0.46  | 0.19  |
| n-heptane     | 1.80  | 1.57  | 1.45  | 1.27  | 1.04  |
| n-octane      | 4.16  | 3.38  | 2.96  | 2.62  | 2.05  |
| n-nonane      | 8.39  | 6.75  | 5.75  | 4.66  | 3.76  |
| n-decane      | 16.06 | 12.48 | 10.16 | 8.02  | 6.15  |
| cyclopentane  | 0.35  | 0.35  | 0.43  | 0.72  | 0.53  |
| cyclohexane   | 1.30  | 1.31  | 1.40  | 1.53  | 1.32  |
| benzene       | 8.43  | 7.82  | 6.84  | 5.64  | 4.52  |
| methyl benzene| 15.27 | 14.11 | 12.08 | 9.75  | 7.38  |
| tetrahydrofuran | 7.28 | 6.62  | 5.94  | 4.99  | 3.96  |
| methanol      | 10.04 | 7.24  | 6.22  | 4.69  | 3.94  |
| ethanol       | 6.82  | 5.41  | 4.30  | 3.33  | 2.52  |
| 1-propanol    | 4.03  | 3.66  | 3.34  | 2.78  | 2.15  |
| isopropanol   | 4.06  | 3.51  | 3.28  | 2.66  | 2.04  |
| acetone       | 6.02  | 5.14  | 4.31  | 3.49  | 2.70  |
| methyl ethyl ketone | 9.30 | 8.21  | 6.99  | 5.55  | 4.21  |
| methyl isobutyl ketone | 12.42 | 11.04 | 10.28 | 8.84  | 7.01  |
| dichloromethane | 6.17 | 4.88  | 4.16  | 3.34  | 2.58  |
| trichloromethane | 6.84 | 6.46  | 5.74  | 4.62  | 3.62  |
| trichloroethylene | 9.45 | 8.30  | 7.00  | 5.58  | 4.47  |

### Table 1. Specific Retention Volumes (\( V_0^s \)) at Different Temperatures (mL·g\(^{-1}\))

| probe solvent | 383 K | 393 K | 403 K | 413 K | 423 K |
|---------------|-------|-------|-------|-------|-------|
| n-hexane      | 0.56  | 0.43  | 0.28  | 0.06  | 0.15  |
| n-heptane     | 0.84  | 1.26  | 1.31  | 1.05  | 1.13  |
| n-octane      | 3.00  | 2.69  | 2.25  | 1.82  | 1.86  |
| n-nonane      | 6.31  | 5.05  | 4.10  | 3.64  | 3.40  |
| n-decane      | 12.42 | 9.90  | 7.54  | 6.42  | 5.29  |
| cyclopentane  | 0.10  | 0.43  | 0.50  | 0.43  | 0.32  |
| cyclohexane   | 1.01  | 1.26  | 0.91  | 0.77  | 0.70  |
| benzene       | 6.07  | 6.08  | 5.44  | 5.25  | 4.36  |
| methyl benzene| 10.81 | 10.43 | 9.82  | 8.99  | 6.98  |
| tetrahydrofuran | 5.27 | 5.08  | 4.72  | 4.60  | 3.92  |
| methanol      | 18.63 | 13.42 | 9.41  | 8.65  | 6.02  |
| ethanol       | 7.36  | 5.48  | 4.35  | 3.71  | 3.08  |
| 1-propanol    | 2.96  | 2.92  | 2.41  | 2.29  | 2.33  |
| isopropanol   | 3.07  | 2.82  | 2.50  | 2.38  | 2.18  |
| acetone       | 5.37  | 4.05  | 3.78  | 3.64  | 2.99  |
| methyl ethyl ketone | 7.53 | 7.14  | 5.91  | 5.19  | 4.33  |
| methyl isobutyl ketone | 8.09 | 7.38  | 6.94  | 6.64  | 6.28  |
| dichloromethane | 5.65 | 4.55  | 3.78  | 3.40  | 2.76  |
| trichloromethane | 5.37 | 5.08  | 4.82  | 4.54  | 3.95  |
| trichloroethylene | 7.05 | 6.78  | 5.94  | 5.50  | 4.48  |
flow rate under ambient conditions, the mass of stationary phase, and the column temperature, respectively. The factor $J$ is calculated using following equation
\[
J = \frac{3}{2} \left( \frac{P_i}{P_0} \right)^2 - 1
\]
where $P_i$ and $P_0$ are the inlet and outlet pressure, respectively.\(^{35}\)

The specific retention volumes of 20 probe solvents on different alkali lignin/ABS blends were determined over the temperature range 383.15–423.15 K (Table 1). $V_g^0$ values decreased with increasing temperature for all probe solvents. Retention diagrams, in which $\ln V_g^0$ was plotted versus $1/T$, for selected probe solvents are shown in Figure 1. The retention diagrams were linear, indicating that there was no phase change in the blends over the temperature range studied. The retention of the probe solvent was, therefore, mainly attributable to adsorption on the solid surface of the alkali lignin/ABS blend.

**Hansen Solubility Parameter.** The determination of the solubility parameter of alkali lignin/ABS blends by the following equation
\[
\left( \frac{\delta_i^2}{RT} - \frac{\chi_{12}^\infty}{V_i} \right) = \left( \delta_1^s \frac{1}{RT} - \frac{\delta_2^s}{RT} \right) \frac{\delta_i^2}{RT} + \frac{\chi_{12}^\infty}{V_i}
\]
where $\delta_1$ and $\delta_2$ are the probe solvent and the stationary phase of the Hansen solubility parameter, respectively, $\chi_{12}^\infty$ and $\chi_{1}^\infty$ are the interaction parameter and the entropy components, respectively.\(^{35}\) $\chi_{12}^\infty$ is calculated by following equation
\[
\chi_{12}^\infty = \ln \left( \frac{273.15 R}{V_i} \right) - \frac{P_i^0}{RT} (B_{11} - V_i) - 1
\]
where $M_i$, $R$, $B_{11}$, $P_i^0$, and $V_i$ are the molecular mass of the probe solvent, the gas constant, the second virial coefficient, the saturated vapor pressure, and the molar volume of the probe solvent, respectively.\(^{35}\)

The correlation of left-hand part and $\delta_i$ was obtained using eq 3 and is shown in Figure 2. Hansen solubility parameters of alkali lignin/ABS blends, $\delta_i$, were calculated by different slopes at 383.15, 393.15, 403.15, 413.15, and 423.15 K, and calculations are shown in Table 2. As seen from the table, the solubility parameters decreased linearly with the increase of temperature. Hansen solubility parameters of alkali lignin/ABS blends with alkali lignin contents of 0, 10, 20, and 30% were 17.40, 19.10, 18.98, and 17.37 (J/cm\(^3\))\(^{0.5}\) at 298.15 K, respectively.

**Dispersion of the Lignin in ABS Resin.** The SEM micrographs of ABS resin and alkali lignin/ABS blends are shown in Figure 3, and a typical microphase-separation structure like a “sea-island” was observed easily. As shown in Figure 3, alkali lignin was uniformly dispersed in the ABS resin matrix, and the interfaces of blends were fuzzy when a little amount of lignin was added. What is more, alkali lignin/ABS blends had smooth surfaces (Figure 8) and the Hansen solubility parameter also increased when the amount of alkali lignin was 10%. The addition of more lignin (20 and 30%) caused the surface to become slightly rougher (Figure 8), and many larger lignin domains and visible interfaces appeared (Figure 3), which suggested that alkali lignin readily agglomerated because of limited interfacial compatibility between alkali lignin and the ABS resin matrix. Bad compatibility also led to the decreasing of the Hansen solubility parameter.

**Quantitative Characterization of the Hansen Solubility Parameter and Tensile Strength of Alkali Lignin/ABS Blends.** The mechanical properties of blends with different proportions of alkali lignin were evaluated. The trends of tensile strength and elongation at break are shown in Figure 4. When a larger amount of lignin was added to the polymer, compatibility and homogenization were very important. As the amount of alkali lignin increased, the tensile strength and elongation at break of the blends decreased gradually, indicating poor compatibility of the phase interface between the ABS resin and alkali lignin and which was attributed to structural and other properties. Although the components of alkali lignin/ABS blends can develop dispersion forces and $\pi$ electron interactions because of the aromatic rings, these interaction forces are weak, resulting in weak bonding forces between the two phases. In the testing process, the lignin is easy to pull out from the ABS resin, as a result, the tensile strength and elongation at break of composites are poor. Additionally, self-interactions among lignin molecules are very strong because of the large number of polar functional groups.
in the molecule. These self-interactions lead to uneven distribution of lignin in the blends. Increasing the amount of alkali lignin in the blend is more likely to cause stress concentration and cracks in the interface.

The correlation between the Hansen solubility parameter and tensile strength was characterized quantitatively and satisfied the variation tendency of quadratic function shown in Figure 5. The correlation of two parameters fitted the binomial relationship

\[
Y = -28.65691 + 1.11229 X - (6.480 \times 10^{-3}) X^2 \quad (69.57 \leq X \leq 101.95),
\]

where \(X\) and \(Y\) are the tensile strength and the Hansen solubility parameter of the blend, respectively. The correlation coefficient was 0.99929. The significance of difference derived from regression model fitting was checked by ANOVA, and values of \(F = 2115.952\) and \(p = 0.015 < 0.05\) were obtained, indicating that \(X\) significantly impacted \(Y\) and that \(R^2\) was statistically significant. There was, therefore, a significant relationship between the Hansen solubility parameter and the tensile strength of the blend.

| alkali lignin content (%) | 383.15 K | 393.15 K | 403.15 K | 413.15 K | 423.15 K | 298.15 K |
|---------------------------|----------|----------|----------|----------|----------|----------|
| 0                         | 15.89    | 15.67    | 15.58    | 15.24    | 15.21    | 17.40    |
| 10                        | 16.56    | 15.93    | 15.85    | 15.22    | 15.37    | 19.10    |
| 20                        | 17.36    | 16.92    | 16.61    | 16.95    | 16.52    | 18.98    |
| 30                        | 16.74    | 16.67    | 16.59    | 16.97    | 16.87    | 17.37    |

Figure 3. Scanning electron micrographs of (A) ABS matrix, (B) ABS-10, (C) ABS-20, and (D) ABS-30.

Figure 4. Effect of different proportions of alkali lignin on \(\delta_2\) and tensile strength and elongation at break.

Figure 5. Tensile strength vs solubility parameter (\(\delta_2\)) of alkali lignin/ABS blends.

Two parameters of blends containing 5 and 25% alkali lignin were determined to check the validity of the regression model. Hansen solubility parameters of blends containing 5 and 25% alkali lignin were 19.20 and 17.49 (J/cm\(^3\))\(^{0.5}\), respectively, and values of tensile strength were 90.08 and 71.68 MPa, respectively (red dots in Figure 5). The values measured roughly satisfied the regression model.

Quantitative Characterization of the Hansen Solubility Parameter and Thermal Weight Loss Temperature of Alkali Lignin/ABS Blends. As the proportion of alkali lignin in the blend increased, the temperature at which thermal weight loss started gradually decreased, likely because of evaporation of low-molecular weight substances in the alkali lignin (Figure 6 and Table 3). The mass retention rate of ABS resin at 600 °C was <1%, indicating that the ABS resin was almost completely oxidized and decomposed at this temperature. However, when alkali lignin was added, the mass retention rate at 700 °C was >7%. Alkali lignin had a
noticeable effect on char-formation and improved the flame retardancy of materials.

When the proportion of alkali lignin in the blend was 10%, the thermal decomposition temperature was 419 °C. This was higher than 412 °C, the thermal decomposition temperature of ABS, and was the highest thermal decomposition temperature of all the blends. These results showed that the addition of alkali lignin to ABS resin improved its thermal stability. When the proportion of alkali lignin was 10%, the Hansen solubility parameter of the blend was also the largest, indicating that thermal stability could be predicted indirectly by the Hansen solubility parameter.

According to Tables 2 and 3, correlation between the Hansen solubility parameter and thermal weight loss temperature was characterized quantitatively and satisfied the variation tendency of quadratic function shown in Figure 7. The correlation of two parameters fitted the binomial relationship

$$Y = -41.07127 + 0.45218X - (8.42 \times 10^{-4})X^2 \quad (217 \leq X \leq 320),$$

where X and Y are the thermal weight loss temperature and the Hansen solubility parameter of the blend, respectively. The correlation coefficient was 0.968. The significance of difference derived from regression model fitting was checked by ANOVA, and values of $F = 46.467$ and $p = 0.103$ were obtained, indicating that there is a very slightly nonsignificant difference.

Two parameters of blends containing 5 and 25% alkali lignin were determined to check the validity of the regression model. Thermal weight loss temperatures of blends with alkali lignin content of 5 and 25% were 291 and 310 °C, respectively (Figure 7). The values measured roughly satisfied the regression model.

### CONCLUSIONS

Hansen solubility parameters and properties of blends with different proportions alkali lignin have been measured, and the correlation between them has also been analyzed quantitatively. Regression models satisfy the variation tendency of quadratic function and has a significant relationship, which is similar with regression models of the polar system of alkali lignin/PVA membranes. What is more, the Hansen solubility parameter increases first and then decreases with the increasing tensile strength and thermal weight loss temperature, providing a reliable basis for on-demand design and performance improvement of ABS/lignin blends.

### EXPERIMENTAL SECTION

**Materials.** Commercial alkali lignin was supplied by Tralin Paper Co., Ltd. (Shandong, China). Alkali lignin was mixed with 0.1 M NaOH, and insoluble material was removed by filtration. HCl (2 M) was added to the filter liquor until the pH value of the liquor fell to 2. The resulting precipitate was removed by filtration, and the filter cake was then washed with distilled water to neutral, dried for 24 h under vacuum, ground to a powder, and set aside. ABS was supplied by Sinopec Sichuan Vinylon Works (Changshou, China), and probe solvents were obtained from Aladdin Industrial Co., Ltd. (Shanghai, China).

**Admeasurement of the Hansen Solubility Parameter by IGC.** Hansen solubility parameters were determined by an Agilent 6890N gas chromatograph (Agilent Technologies, Santa Clara, CA, USA), equipped with a flame ionization detector. The injector and detector were operated at 200 °C. High purity nitrogen was used as the carrier gas, and the nitrogen flow rate was maintained at 20 mL/min. Solvent-rinsed stainless steel chromatography columns (2000 mm, 1/8 in. O.D.) were packed with Chromosorb 6201 that had been coated with mixtures of alkali lignin and ABS using concentrated acetone solutions. The columns packed were

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**Table 3. Effect of Lignin Content on Thermal Weight Loss Temperature of Alkali Lignin/ABS Blends**

| proportion of alkali lignin (%) | 0  | 10 | 20 | 30 |
|-------------------------------|----|----|----|----|
| thermal weight loss temperature (°C) | 320 | 246 | 238 | 217 |

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**Figure 6.** Thermogravimetric and differential scanning calorimetry curves of alkali lignin/ABS blends.

**Figure 7.** Solubility parameter ($\delta_2$) vs thermal weight loss temperature of the alkali lignin/ABS blend.
treated at 130 °C for about 8 h by gas chromatography. Probe solvents were injected by a 0.5 μL special syringe to measure retention times at 383.15, 393.15, 403.15, 413.15, and 423.15 K. Each solute probe was injected at least three times, and the average retention time, t_r, was used to calculate Hansen solubility parameters of the alkali lignin/ABS blends.

Preparation of Alkali Lignin/ABS Blends. ABS resin particles were ground to a 100 mesh powder using a small pulverizer. Alkali lignin was then added to the ABS powder to provide blends with 10, 20, and 30 wt % alkali lignin. The blends were molded into test samples (Figure 8), following the standards set out in GB/T 1040.2-2006. The samples were treated according to GB/T 1040.2-2006. The samples were treated according to GB/T 1040.2-2006. The temperatures in the cylinder and cavity were 200 and 50 °C, respectively.

SEM Testing. The TM3030 scanning electron microscope (TM3030, Hitachi, Japan) was used to observe the dispersion and compatibility of alkali lignin in the ABS matrix on the fractured surfaces of samples at an accelerating voltage of 10 kV.

Test of Mechanical Properties of Alkali Lignin/ABS Blends. The mechanical properties of the alkali lignin/ABS blends were measured according to the standards set out in GB/T 1040.2-2006. The samples were treated according to GB/T 2918-1998. Tensile strength of blends was tested by a universal testing machine (LDX-200, Beijing Landmark Packaging Material Co., Ltd., Beijing, China) at a speed of 50 mm/min, and an average of five measurements was recorded for each sample.

Test of Thermal Properties of Alkali Lignin/ABS Blends. Samples were analyzed using a Q50 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA) over the temperature range 25–800 °C, with a scanning rate of 10 °C/min and a nitrogen flow rate of 10 mL/min. Then, samples were then analyzed using a Q20 differential scanning calorimeter (TA Instruments) over the temperature range 25–300 °C, with a scanning rate of 10 °C/min and a nitrogen flow rate of 10 mL/min.

Figure 8. Shape of the blends. (a) ABS; (b) 10% alkali lignin/ABS; (c) 20% alkali lignin/ABS; and (d) 30% alkali lignin/ABS.

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