

## Evaluation of curing and thermal behaviors of konjac glucomannan-chitosan-polypeptide adhesive blends

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**ABSTRACT:** An environmentally friendly wood adhesive has been achieved through novel blending of konjac glucomannan and chitosan with polypeptide. Tensile tests reveal an optimal curing temperature of 130°C. Both viscoelastic properties of the adhesive blends during curing process, and the structural variation of chemical components induced by curing temperature, were defined by using dynamic rheometry, X-ray photoelectron spectroscopy, and Fourier transform infrared spectroscopy. Results show both storage and loss modulus increase markedly from 90 to 105°C because of the reactions occurred between konjac glucomannan, chitosan, and polypeptide with formation of amide. Increased polypeptide content not only strengthens intermolecular hydrogen bonds but also enhances covalent reactions occurred between the components. Thermogravimetric and differential scanning calorimetry analyses indicate good miscibility of components in the adhesive blends and improved thermal stability with added polypeptide. Hydrogen bonds between polysaccharides and polypeptide break at 125 ± 10°C. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42202.

**KEYWORDS:** adhesives; blends; mechanical properties; thermal properties; thermosets

Received 27 September 2014; accepted 16 March 2015

DOI: 10.1002/app.42202

### INTRODUCTION

Adhesives originating from natural materials have been widely used throughout history. From the 1970s, these natural adhesives were replaced by petrochemical adhesives for their numerous advantages, such as easy handling and good bond strength. With exhaustion of fossil resources and rising environmental concerns, future use of petrochemical resins appears limited.

Previous research indicates that the abundance, low cost, and nontoxicity in biomass makes it an excellent raw material choice for adhesives. Biomass includes starch,<sup>1</sup> soy flour,<sup>2,3</sup> whey protein,<sup>4</sup> lignin,<sup>5,6</sup> tannin,<sup>7</sup> and konjac glucomannan.<sup>8,9</sup> Konjac glucomannan (KGM) is one of the most abundant natural polymers, consisting of  $\alpha$ -glucose and  $\alpha$ -mannose in a molar ratio of 1.6 : 1.0.<sup>10</sup> Because of its poor water resistance, KGM has rarely been used independently as wood adhesive. Attempts have been made in wood bonding<sup>11</sup> to modify KGM with chitosan, which is a cationic polysaccharide biopolymer composed primarily of  $\beta$ -(1-4)-2-amino-2-deoxy-D-glucopyranose units. When blending KGM with chitosan as a wood adhesive,<sup>8,12</sup> the thermostability and bond strength in both dry and wet states improve.

Polypeptides consist of several amino acid molecules linked by a peptide bond and have low relative molecular weights. Our pre-

vious research demonstrates that polypeptide's amine and carboxyl groups enable reaction with aldehyde and amine groups located in KGM and chitosan, improving both bond strength and moisture resistance.<sup>13,14</sup> On the basis of these observations, a novel wood adhesive combining KGM, chitosan, and polypeptide has been developed. The viscoelasticity, mechanical properties, as well as the relationship between structure and mechanical properties of the adhesive blends have been investigated previously.<sup>13</sup> As a supplement to our previous research, the critical curing mechanism for industrial processing parameters need to be further investigated. This study clarifies the curing behavior of KGM-chitosan-polypeptide adhesive blends, by investigating viscoelastic properties during curing, plus chemical structural variations cured at different temperatures. We also studied the physicochemical variations and changes in thermal behavior induced by addition of the polypeptide. The optimal curing temperature was determined using tensile tests.

### EXPERIMENTAL

#### Materials

Konjac glucomannan (water-soluble polysaccharide, 100 mesh) was provided by Qindong Konjac Food Co. (China) with a viscosity of 10 Pa·s (water solution, solid content 1% w/v). The

**Table I.** Nomenclature of the Adhesive Blends by Polypeptide Concentration

Nomenclature	Konjac glucomannan (w/v, %)	Chitosan (w/v, %)	Polypeptide (w/v, %)	Glacial acetic acid (v/v, %)
KCP-0	2.50	2.50	0.00	2.00
KCP-1.5	1.75	1.75	1.50	2.00
KCP-2.0	1.50	1.50	2.00	2.00

viscosity-average molecular weight of  $2.45 \times 10^6$  Da was calculated according to the Mark–Houwink equation<sup>15</sup> with glucomannan content above 95%. Chitosan (80 mesh,  $M_w$   $3.74 \times 10^5$  Da), obtained from Golden-Shell Biochemical Co. (China), has a deacetylation degree of 95% with a viscosity of 1.2 Pa·s in 2% (v/v) acetic acid solution at 1% concentration. Powdered collagen extracted (>99% polypeptide content;  $M_w$   $3.0 \times 10^3$  Da; Gly 24.17%, Glu 11.29%, Ala 9.51%, Arg 8.88%, Asp 7.01%, Hyp 6.45%, Lys 3.90%, Pro 4.41%, Ser 3.76%, Leu 3.68%, Val 3.52%, Cys 3.90%, Thr 3.36%, Phe 3.03%, Ile 2.30%) was purchased from Shaanxi Fusen Biotechnical Co. (China). Tests show a viscosity of 0.1 Pa·s (water solution, solid content 1% w/v) for the collagen extract. All other chemicals were commercially sourced and analytical-grade, applied without further purification.

#### Adhesive Blend Preparation and Membrane Casting

Chitosan and polypeptide were first weighed and dissolved in distilled water for 15 min by machine at ambient temperature. Because chitosan will only dissolve in acidic solution, glacial acetic acid was added by drop while stirring for 10 min., then degassed. After 4 h of gelatinization, KGM was added slowly and steadily over 15 min. while stirring to obtain a clear and homogeneous polymer solution. The nomenclature and concentrations of samples used in this study are shown in Table I. KCP-2.0 was the adhesive with optimal formulation. A control sample of KGM–chitosan adhesive blends was also prepared following the above process without the addition of polypeptide. The solid content of these adhesives was 5% (w/v).

Adhesive blends were cast onto a clean glass plate and cured at 130°C by oven with replicate samples cured at 25°C for reference. The resulting membranes were then peeled from the glass plate. The average thickness of these films was measured at  $0.53 \pm 0.16$  mm.

#### Tensile Tests

Using the Chinese national standard method GB/T 9846.3–2004, poplar (*Populus spp.*) veneer sections of 1.5 mm thick with a moisture content of 12% (conditioned) were rotary cut to test tensile strength. Each  $15 \times 15$  cm veneer received a single-sided coat of 25 g/m<sup>2</sup> solid adhesive content. The veneers were then assembled with the center veneer grain perpendicular to the two face veneers. The mat was first pressed under 0.5 MPa at ambient temperature for 24 h, followed by hot pressing in a DXL1500 (Xianyang Weidi Co., China) under 3 MPa at a set temperature (110, 120, 130, or 140°C) for 15 min. The resulting panels were further conditioned at a relative humidity of  $50 \pm 2\%$  and ambient temperature for at least 7 days. The panels were then cut as shown in Figure 1. Tensile strength in

dry and wet (boiled in water at 60°C for 3 h) states of 12–20 replicas were then tested using a versatile electronic tensile tester (CMT-5504, Shenzhen Sans Test Machine Co., China) at a speed of 3 mm/min.

For the tensile strength of blend films, Chinese national standard method (GB 13022-91) was used. Films were conditioned at 20°C with a relatively humidity of 36% before testing. The testing speed of 3 mm/min was applied, and at least 10–20 replicas of each type were tested.

#### Water Solubility Index of Blend Film

The water solubility was measured based on the method proposed by Gontard *et al.*<sup>16</sup> Each film ( $15 \times 15$  mm) was weighted, immersed in a beaker with 50 mL distilled water, and gently shook for 24 h at ambient temperature. After that, solutions in beakers were passed through a filter paper. The insoluble fraction was dried in an oven at a temperature of 105°C until it reached a stable weight to calculate the water-soluble matter as a percentage of the initial weight. Triplicate measurements were performed.

#### Viscoelasticity Dependence on Temperature

Using a stress-controlled rheometer during curing (AR 2000ex, TA Instruments Rheology Division), with a parallel plate geometry (25 mm diameter) at a gap of 1 mm, we performed viscoelasticity analysis. Samples were loaded onto the rheometer both with and without a coating to the periphery of silicone oil to minimize water evaporation. In temperature ramp measurements, the storage and loss modulus were recorded from 25 to 140°C at a heating rate of 3°C/min. with a frequency of 1 Hz. The tests were performed in triplicate within the linear viscoelastic region.

#### Viscosity Properties under Steady Shear

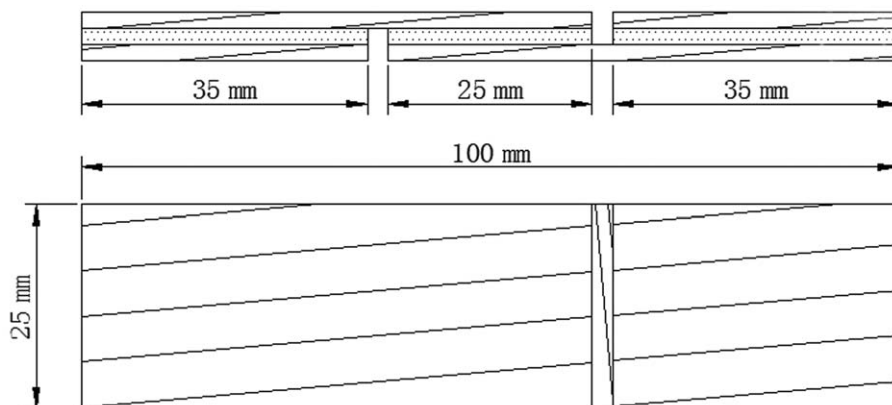
Apparent viscosity data collected at shear rates from 0.01 to 1000 s<sup>-1</sup> at 25 and 80°C were then fitted into the Cross model, an equation describing the whole flow curve of non-Newtonian fluid,<sup>17</sup> as shown in eq. (1):

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (K\dot{\gamma})^n} \quad (1)$$

Here,  $\eta$  is the apparent viscosity at a given shear rate  $\dot{\gamma}$ ,  $\eta_0$ , and  $\eta_{\infty}$  are the zero and infinite shear rate viscosities, respectively.  $K$  is associated with the structural relaxation time and has the dimensions of time, and  $n$  is the flow behavior index (dimensionless).

#### Fourier Transform Infrared Spectroscopy Analysis

The pulverized blend films were analyzed at ambient temperature using compressed pellets of potassium bromide (KBr) in



**Figure 1.** Form and dimensions of a specimen for tensile test.

the range of 400 to 4000  $\text{cm}^{-1}$  on an FT-IR Avatar 330 (Nicolet Corp., USA).

#### X-ray Photoelectron Spectroscopy Analysis

X-ray photoelectron spectroscopy (XPS) characterization of blend films was performed with a spectrometer Thermo scientific K-Alpha (Thermo Fisher Scientific, UK) equipped with monochromatic Al-K $\alpha$  source. Survey spectra were gathered using an average of five scans with a pass energy of 200 eV and running from 1350 to 0 eV. High-resolution spectra of N 1s region were recorded with a pass energy of 50 eV and a step size of 0.1 eV. The peaks were decomposed into subcomponents using a Gaussian (80%)–Lorentzian (20%) curve fitting program. Electron binding energies were calibrated to the hydrocarbon C 1s at 284.6 eV. A  $\Delta$ BE of 0.5 eV is significant.

#### Thermogravimetry Analysis

Using a TGA Q500 (TA Instruments, USA), we analyzed the blend films, each weighing 6–8 mg. The weight change of samples was scanned from 25 to 300°C under a nitrogen atmosphere (30 mL/min) at heating rate of 3°C/min.

#### Differential Scanning Calorimetry Measurements

Differential scanning calorimetry (DSC) analysis of the blend films was conducted under a nitrogen atmosphere at flow rate of 25 mL/min on a DSC Q2000 (TA Instruments, USA) from 0 to 300°C at a heating rate of 3°C/min. Aluminum sample pans containing sliced films 6–8 mg were hermetically sealed with an empty pan as a reference, replicated three times.

## RESULTS AND DISCUSSION

#### Effects of Curing Temperature on Tensile Strength

Thermosetting adhesives are heat-sensitive; indeed, they are cured by heating. Based on curing temperatures depicted in Figure 3, a group of set temperatures (100, 110, 120, 130, and 140°C) were used to evaluate the effects of curing temperature on bond strength as presented in Figure 2(a).

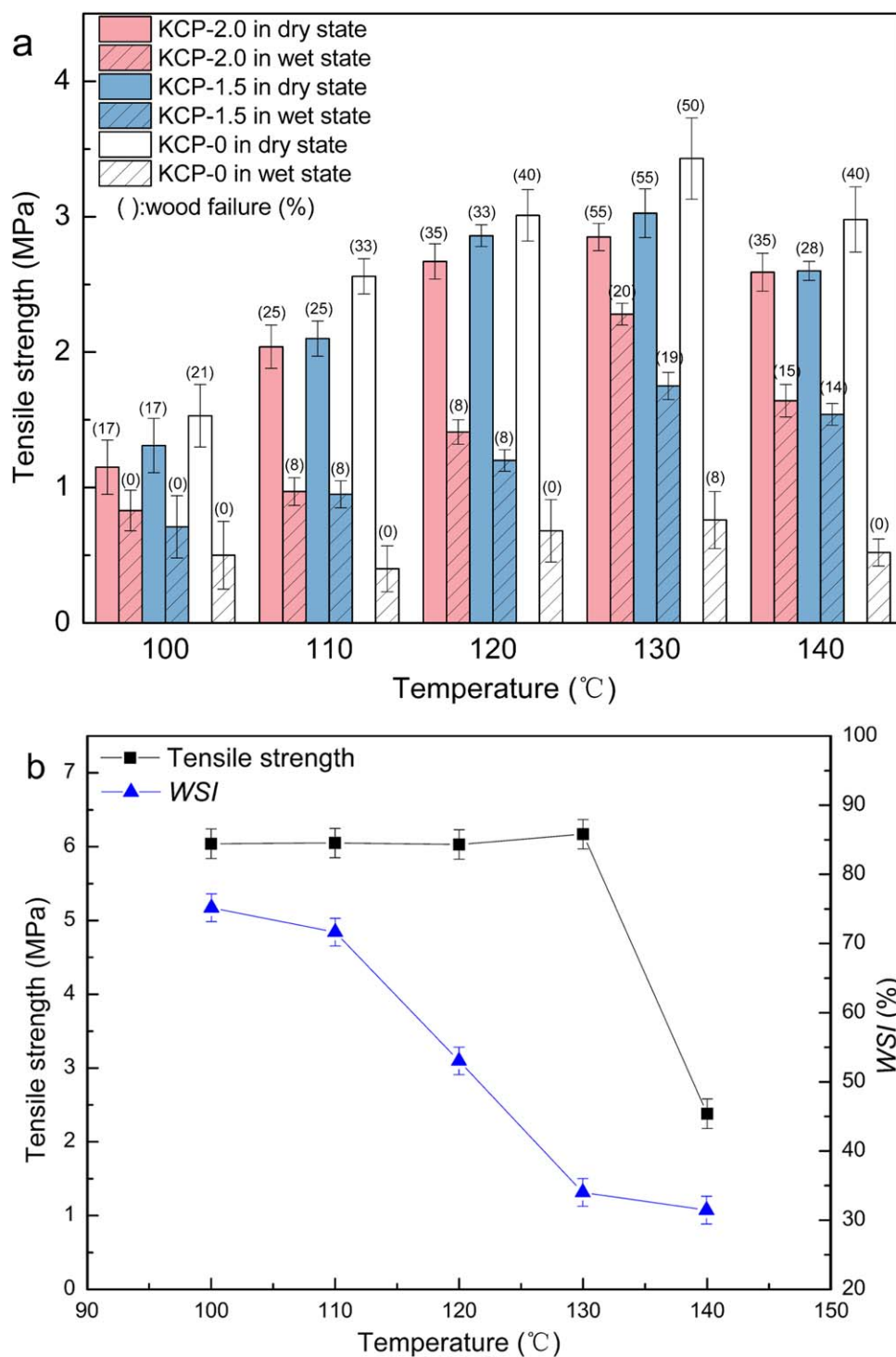
It was observed in all formulations, the tensile strength in both dry and wet states increases with curing temperature from 100 to 130°C [Figure 2(a)]. Bond strength of the plywood is determined by the strength of bond line and interfacial adhesion, and wettability and penetrability of the adhesive have great effect on interfacial adhesion. The increase of the curing temperature not only

helps rapid removal of water residues, reduces the minimum viscosity of the adhesive to improve its penetration, but also accelerates reactions among the components of the adhesive to form a coherent adhesion interface and a compact bond line, contributing to the improvement in tensile strength. At a curing temperature of 140°C, reduced tensile strength was observed.<sup>17</sup> No peak was observed in either DSC (Figure 8) or DTG (Figure 7) curves of KGM, chitosan or polypeptide at 140°C. For KCP-1.5 and KCP-2.0, endothermic peaks were observed in DSC curves, whereas no degradation was observed in DTG curves at about 140°C, demonstrating that the breakage of hydrogen bonds between KGM, chitosan, and polypeptide which weakened the structure of bond line may be responsible for this decrease. Yet breakage of hydrogen bonds between KGM and chitosan was the reason for the decrease in KCP-0. Moreover, high-temperature-accelerated curing may lead to incomplete reactions among the components of adhesive, as well as reduced entanglement of polymer chains in the adhesive with wood fiber, thus negatively affecting adhesion. Because water molecules can penetrate into wood and act as a plasticizer for hydrophilic polymers in the same way as other polysaccharide-based adhesives,<sup>1</sup> the tensile strength of the adhesive blends would unavoidably decrease after immersing in water.<sup>13</sup> Wood failure was much lower in wet state and can be improved by polypeptide addition [Figure 2(a)].

The mechanical properties of the bond line are closely related to bond strength of the plywood. Therefore, tensile strength and water solubility of films KCP-2.0 cured at different temperatures were investigated and shown in Figure 2(b). Tensile strength remained approximately invariant when cured at 100, 110, and 120°C, then reached a maximum at 130°C, suggesting a strengthened structure was obtained in bond line when cured at 130°C. Films were crisp in texture when cured at 140°C, resulting in the reduction in tensile strength. The water solubility decreased with the increase in curing temperature, demonstrating the water resistance of bond line and reactions between components of the adhesive were improved by rising temperature. In accordance with the results of tensile tests of plywood, 130°C is the optimal curing temperature.

#### Viscoelastic Behavior of Adhesive During Curing

The same as other thermosetting adhesives, the KGM–chitosan–polypeptide adhesive blends are viscous liquids which tend to

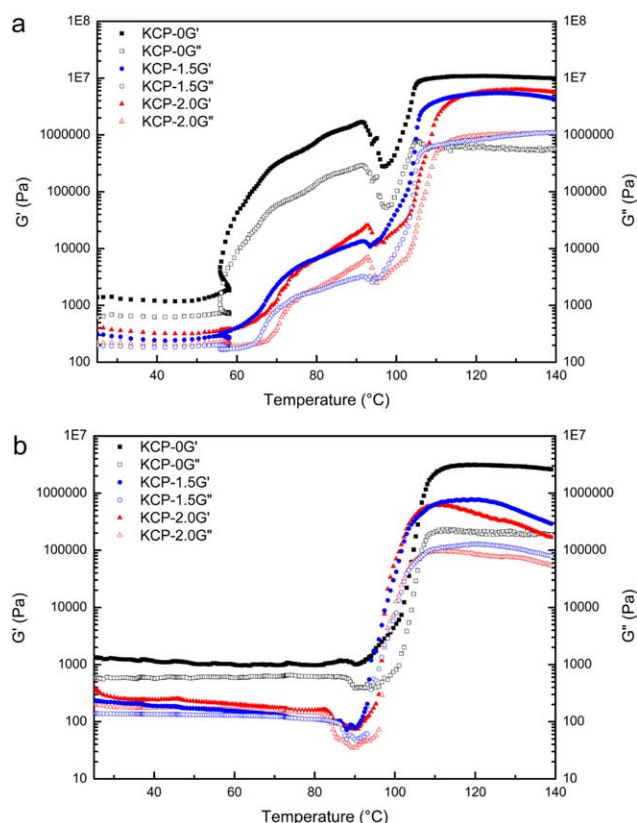


**Figure 2.** Tensile strength of (a) KGM-chitosan-polypeptide adhesive blends and (b) films KCP-2.0 cured at different temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

cure into highly rigid solids. To best understand changes in structure and determine the ideal pressing temperature, evaluation of viscoelastic behavior during curing is essential. As shown in Figure 3, storage modulus ( $G'$ ) higher than loss modulus ( $G''$ ) in all samples over the entire experimental range indicates the behavior of an elastic bulk.

Progressive reduction is followed by a slight increase in the values of  $G'$  between 25 and 57°C with values of  $G''$  remaining fairly constant, which is attributed to the increase of molecular thermal motion, although structural conformation remains stable [Figure 3(a)]. Further temperature increase induces marked development in the elastic modulus for all the adhesives, which



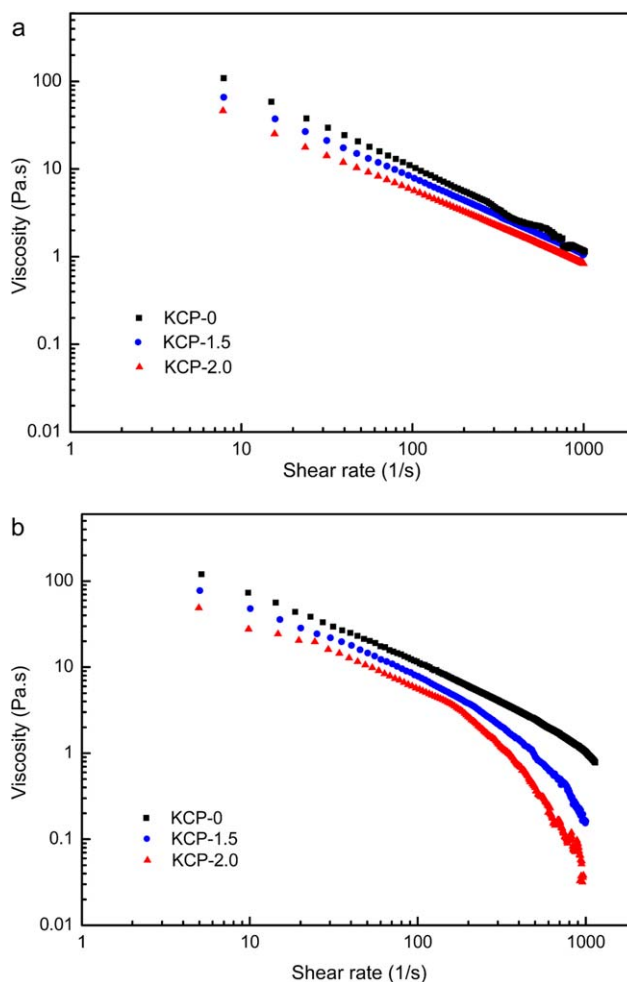


**Figure 3.** The temperature dependence of storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of adhesive blends (a) uncovered and (b) covered with silicon oil. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

achieves a maximum of 1.7 MPa, 13.4 kPa, and 26.0 kPa at 93, 96, and 97°C for KCP-0, KCP-1.5, and KCP-2.0, respectively. Modulus's increase results from enhanced entanglement of chain segments. Macromolecules have the ability to bond neighboring molecules and form a network structure, whereas thermal motion encourages molecules to traverse neighboring chains and form new junction zones. Water in both free and bound states is the primary constituent of adhesive blends. Water evaporation concentrates the sample with increased temperature and significantly improves chain entanglement. Further heating to 95°C decreases the modulus slightly as hydrogen bonds between the molecular chains are partially destroyed.<sup>18</sup> The minimum pre-curing modulus occurs, which indicates the onset of curing. Increase in KGM–chitosan concentration is in direct proportion to decrease in modulus, suggesting polypeptide stabilizes the structure of adhesive by physically entangling chain segments freed by breakage of hydrogen bonds. The modulus profiles show a sharp up-turn followed by a plateau region as the temperature continues to increase, which represents the completion of curing. The complete evaporation of water reduces the size of the interstices between neighboring chain segments<sup>19</sup> to enhance the physical entanglement; furthermore, that high temperature provides sufficient energy to carry out covalent reactions among the components, which could be responsible for the sharp increase in the elastic modulus. The final modulus of KCP-0 is much higher, indicating that the long molecular chains

of KGM and chitosan contribute to the stiffness of the elastic matrix structure. KCP-1.5 has a lower final modulus value than KCP-2.0, demonstrating that higher polypeptide content is conducive to forming a higher density structure, which does not readily breakdown. It should be noted about Figure 3(a) that a decrease in temperature was observed near 57°C, which indicates existence of an endothermic process. Evaporation of water and breakage of hydrogen bonds between components and water are energy-absorption processes, to be discussed further in the thermal analysis.

As evaporation of water is minimized by silicon oil, the storage and loss modulus of KCP-0, KCP-1.5, and KCP-2.0 changes slightly between 25 and 87°C, as shown in Figure 3(b). Comparing their modulus with that shown in Figure 3(a), onset temperatures of curing were lower and final modulus values were much smaller. For samples without silicon oil coverage, continuous evaporation of water during curing facilitates the covalent reactions, which generates the higher final modulus and helps to form more compact structures.



**Figure 4.** Flow curves of KGM–chitosan–polypeptide adhesive blends with 0, 1.5, and 2.0% polypeptide contents at (a) 25°C and (b) 80°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table II.** Effect of Temperature on the Rheological Parameters of the KGM–Chitosan–Polypeptide Adhesive Blends

	25°C			80°C		
	K(s)	<i>n</i>	<i>R</i> <sup>2</sup>	K(s)	<i>n</i>	<i>R</i> <sup>2</sup>
KCP-0	848.90	0.96	0.99	1.30	0.88	0.99
KCP-1.5	0.94	0.88	0.99	0.03	1.64	0.73
KCP-2.0	1.22	0.84	0.99	0.43	1.63	0.61

### Flow Behavior of Adhesive Blends under Steady Shear

As modulus changed markedly between 25 and 80°C [Figure 3(a)], the flow behavior of adhesive blends under steady shear was found to illustrate changes in structure induced by rising temperature. A marked shear-thinning behavior was observed for all samples as presented in Figure 4. Increasing the shear rate decreases the extent of chain entanglement and thus decreases the viscosity.

Curves of the adhesives detected at 25°C fit the Cross model well [as shown in eq. (1)] with high correlation coefficients ( $R^2 > 0.99$ ). When this model is used to describe non-Newtonian liquids, the value of *n* dictates the degree of shear thinning, with a higher value indicating decreases in the flexibility of the molecules and increases in stiffer conformation.<sup>19</sup> As shown in Table II, values of *n* are inversely proportional to polypeptide content, indicating that KGM and chitosan hold the inflexible back-bone conformation. When shear is at 80°C, the Cross model fails to describe the flow behaviors of KCP-1.5 and KCP-2.0, whose viscosities at high shear rates are much lower than those in curves at 25°C. Viscosity is proportional to the extent of entanglement of chain segments which in turn depends on the type of polymer, molecular weight, concentration of polymer, temperature, and shear rate. Decreased KGM–chitosan content induces weakened entanglement, which composes the adhesive structural backbone. Network structure of adhesive blends readily break down under high shear rates at 80°C causing the marked decrease in viscosity. KCP-0 still fits the Cross model at 80°C and almost overlaps the flow curve at 25°C, which can be ascribed to the high KGM–chitosan content. Most of these long molecular chains are curled when dispersed in a high-density solution. When shear rate is high, the curly molecular chains straighten to disperse the shear force, avoiding breakage of the network structure.

With the addition of polypeptide, viscosity decreases either at 25 or at 80°C. Total solid content for the three samples were all equal, yet polypeptide had much lower molecular weight and viscosity than KGM and chitosan. Therefore, the viscosity decreases with increasing polypeptide content.

### Fourier Transform Infrared Spectroscopy Analysis

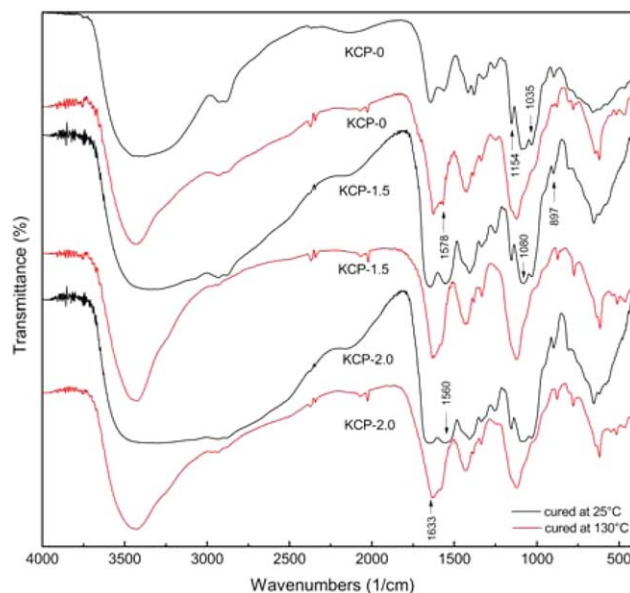
Comparing the Fourier transform infrared spectroscopy (FTIR) spectra of blend films cured at 130°C to those cured at 25°C (Figure 5), the intensity of peaks at about 1578  $\text{cm}^{-1}$  decreases, due to the Maillard reaction, which consumes amino groups and reducing ends in sugars when exposed to 130°C. The peak of amide I shifts from 1648 to 1633  $\text{cm}^{-1}$ , amide II peak from about 1560 to 1578  $\text{cm}^{-1}$ , and the peak at 1371  $\text{cm}^{-1}$ , assigned

to the characteristic bent absorption band of amino groups, as well as the stretching of amide III, shifts to lower wavenumbers. This was attributed to enhanced hydrogen bonding between the –NH and the –C=O groups<sup>20</sup> induced by curing at high temperature. The peaks at 1154, 1080, 1035, and 897  $\text{cm}^{-1}$  that are assigned to the C–O stretch and the  $\beta$ -D-configuration<sup>21,22</sup> disappeared, suggesting the breakage of sugar units during curing at 130°C and proving the presence of the Maillard reaction.<sup>23</sup> For spectra cured at 130°C, the intensity of peaks at 1578  $\text{cm}^{-1}$  also decreased with increasing polypeptide addition. Although rise in amino group concentration facilitates the Maillard reaction, the consumption of amino also increases, leading to the decrease in intensity.

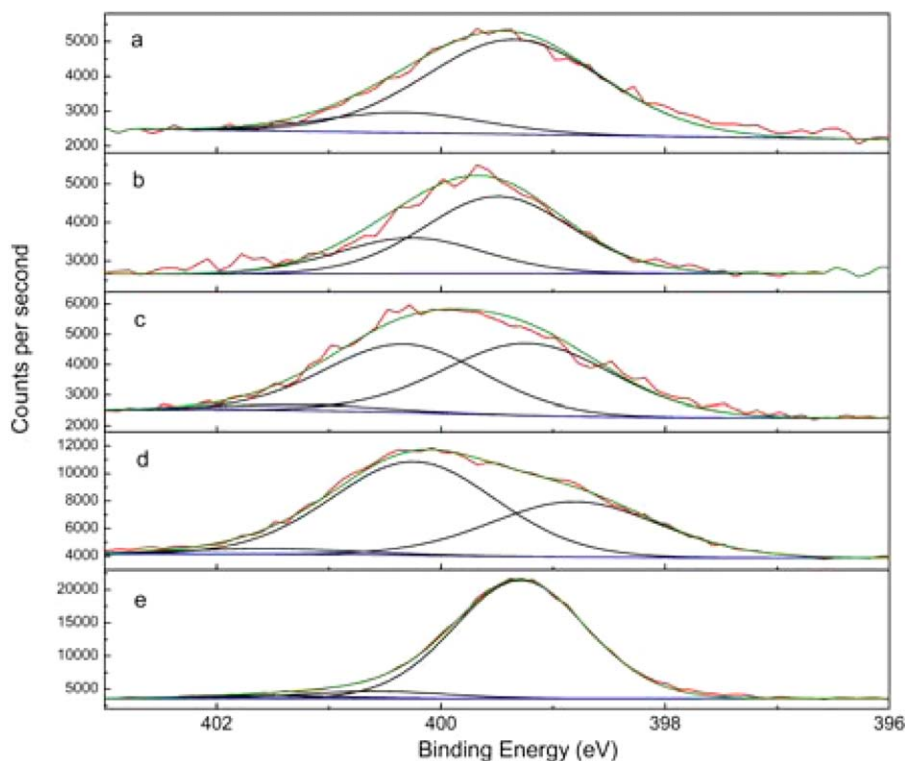
### XPS Analysis

Reactions between –NH<sub>2</sub>, –COOH, and –CHO located on either KGM, chitosan, or polypeptide with formation of amide have been detected in our previous research.<sup>14</sup> KCP-0 and KCP-2.0 cured at different temperatures were characterized by the photoemission bands N 1s to investigate chemical reactions induced by curing at 130°C and polypeptide addition. The N 1s signal were decomposed as shown in Figure 6, and the binding energies (BE) and their assignment of the peaks are included in Table III.

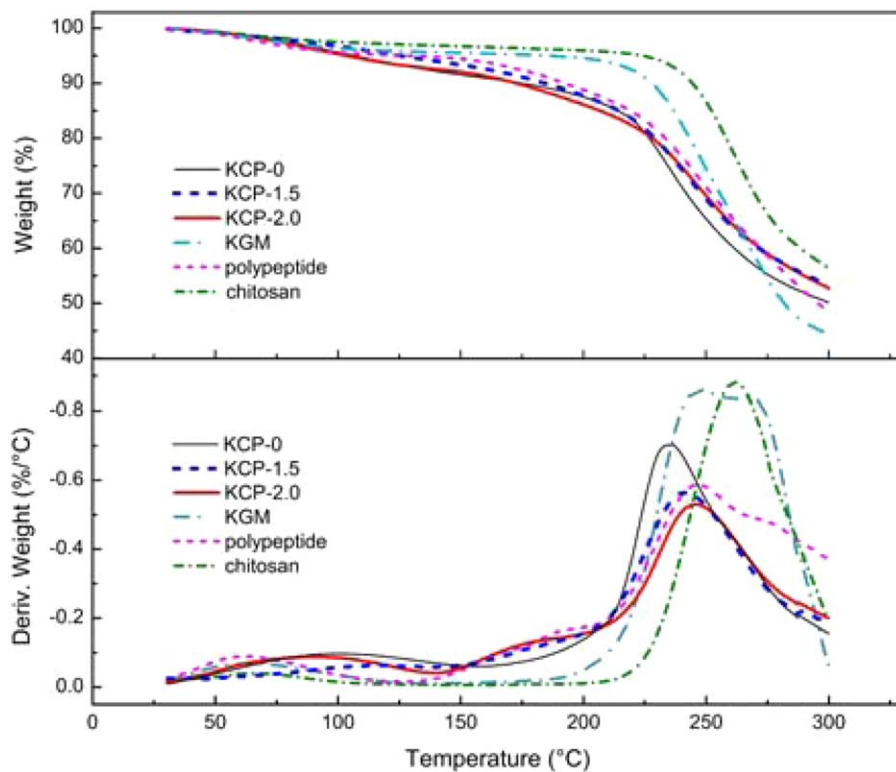
O=C–NH was observed in all the samples. Compared samples cured at 130°C with those cured at 25°C, significant amounts of O=C–NH was formed and the atomic concentration (AC) increased markedly, indicating that curing at 130°C enhances those covalent reactions among the components. With the addition of polypeptide, the atomic concentration of amide in blend films also increased compared to KCP-0 and polypeptide. Structure of the adhesive blends was strengthened by curing at



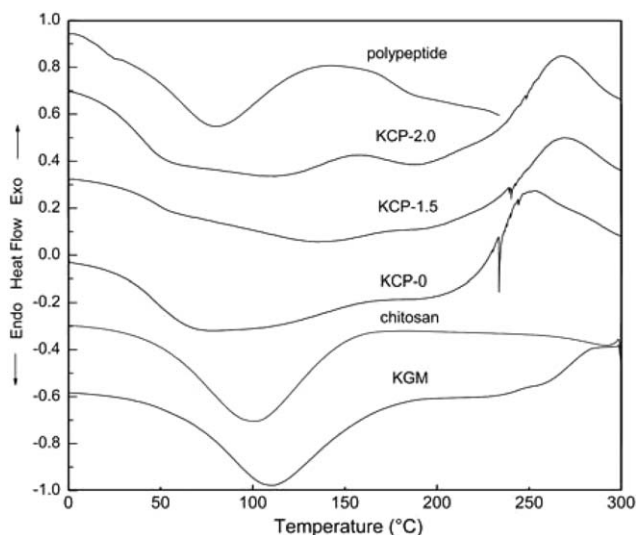
**Figure 5.** FTIR spectra of KGM–chitosan–polypeptide blend films cured at 25 and 130°C with 0, 1.5, and 2.0% polypeptide contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 6.** N 1s spectra of films: (a) KCP-0 cured at 25°C, (b) KCP-0 cured at 130°C, (c) KCP-2.0 cured at 25°C, (d) KCP-2.0 cured at 130°C, and (e) polypeptide. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** Thermogravimetric analysis curves of pure KGM, chitosan, polypeptide, and their blend films cured at 130°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** DSC curves of pure KGM, chitosan, polypeptide, and their blend films cured at 130°C.

130°C, resulting in the smaller *WSI* of film and improved bonding performance of the plywood in wet state.

#### Thermogravimetric Analysis

Thermogravimetric analysis results, as shown in Figure 7, evidence the strengthening of adhesive structure by polypeptide addition. After the first-stage loss of moisture at low temperature (below 115°C), the majority weight loss occurs above 200°C due to a complex process, including degradation of polysaccharide rings<sup>24</sup> and disintegration of polypeptide.<sup>25</sup> During rapid weight loss, onset of decomposition for KGM, chitosan, and polypeptide occurs at 225, 235, and 206°C, respectively. However, the decomposition onset point for KCP-0 is 215°C, lower than that found for KGM and chitosan. This indicates a reduction in thermal stability owing to the Maillard reaction process, which forms Schiff bases.<sup>26</sup> When a polypeptide was added to the KGM–chitosan blend, the onset temperature of major weight reduction increased in tandem with polypeptide content. The maximum degradation occurs at 234, 243, and 245°C for KCP-0, KCP-1.5, and KCP-2.0, respectively, which indicates the enhanced thermal stability induced by the increasing addition of polypeptide. Furthermore, the covalent reactions occurred during curing at 130°C form various compounds. When blend films were heated on a thermogravimetry, the degradation of polypeptide or substances originated from the

covalent reactions may be responsible for the stage ranging from 140 to 200°C on the DTG curves. All the blends exhibited a single degradation temperature in their DTG curves, which may indicate that KGM, chitosan, and polypeptide have good compatibility.

#### DSC Measurements

The DSC studies on the pure KGM, chitosan, and polypeptide, as well as their blend films were performed to correlate structural changes with increasing temperature (Figure 8). Results show the first endothermic peak from 50 to 110°C, which was attribute to moisture-mediated disorganization of crystallites, as well as loss of water molecules. When blending KGM and chitosan with polypeptide, endothermic peaks appeared at 115 and 135°C for KCP-2.0 and KCP-1.5, respectively. However, no peak was observed in the DTG curves at these temperatures, suggesting that breakage of hydrogen bonds between polysaccharides and polypeptides may be responsible for the absorption of heat. Comparing the curves of DSC with DTG (shown in Figure 7), the exothermic peaks at 233, 240, and 248°C for KCP-0, KCP-1.5, and KCP-2.0 correspond well with their respective maximum degradation rate temperature. Therefore, these exothermic peaks result from the thermal decomposition of hydrogen bonds and glycosidic bonds in polysaccharides<sup>20</sup> as well as depolymerization of some component. Furthermore, no exothermic peak was observed at temperature between 200 and 250°C in DSC curves of KGM and chitosan, also indicating an decreased thermal stability after blending in accordance with that found in TGA. With increasing polypeptide content, these peaks shift to a higher temperature and diminish remarkably, which indicates that the reactions between polysaccharides and polypeptide enhance thermal stability of the blend films. Polypeptide addition yields good miscibility and enhanced thermal stability, proven by a unique exothermic peak which shifts to a higher temperature with increasing polypeptide content, according with results of thermogravimetric analysis. Changes to the number and location of the endothermic and exothermic peaks in the curves of pure materials and adhesive blends indicate the formation of hydrogen bonds and the existence of reactions among KGM, chitosan, and polypeptide.

#### CONCLUSIONS

An environmentally friendly wood adhesive was prepared by blending KGM, chitosan, and polypeptide. Curing mechanism that was crucial for industrial application was investigated

**Table III.** Assignments of N 1s Spectral Based on the Binding Energies (BE) and the Atomic Concentration (AC) for Polypeptide, Films KCP-0 and KCP-2.0 Cured at Different Temperature

		C-NH <sub>2</sub>		O=C-NH		C-NH <sub>3</sub> <sup>+</sup>	
		BE (eV)	AC (%)	BE (eV)	AC (%)	BE (eV)	AC (%)
25°C	KCP-0	399.33	83.33	400.33	16.67		
	KCP-2.0	399.23	51.02	400.33	45.41	401.22	3.57
130°C	KCP-0	399.44	68.49	400.26	31.51		
	KCP-2.0	399.02	36.53	400.24	59.88	401.54	3.59
	Polypeptide	399.29	90.91	400.60	6.36	401.55	2.73



through physicochemical variations of the adhesive blends cured at different temperatures. Curing of the adhesive blends is a complicate process combining evaporation of water, entanglement of chain segments, and formation of intermolecular hydrogen bonds and amide between  $-CHO$ ,  $-NH_2$  and  $-COOH$  located on either KGM, chitosan or polypeptide. Meanwhile, intermolecular hydrogen bonds existed among the components are enhanced by increasing polypeptide content. Thermal decomposition of the adhesive blends occur at  $240 \pm 8^\circ\text{C}$ . Good miscibility of components exists in blend films, and thermal stability is enhanced with the increasing addition of polypeptide. This study provides fundamental information for industrial applications of this novel wood adhesive and contribute to more effective utilization of these natural polymers.

#### ACKNOWLEDGMENTS

The authors are grateful to the Special Fund for Agro-Scientific Research in the Public Interest of China for its financial support (Grant No. 201003063-07) and the Fundamental Research Funds for the Central Universities (NO. BLX2013003).

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