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# Improvement of the Physical Properties of Paper Sheet-lignophenol Composites Prepared Using a Facile Impregnation Technique

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Lignophenol was separated from bamboo (*Sinocalamus affinis*) using a phase separation system. Different concentrations of a lignophenol-acetone solution were used to impregnate hardwood pulp fiber sheets (80 g/m$^2$). The results showed that the tightness, tensile index, tear index, and burst index properties of sheets impregnated with a lignophenol acetone solution (80 g/L) increased 5.66%, 160.08%, 93.66%, and 140%, respectively, compared with sheets prepared without lignophenol. The lignophenol-hardwood pulp fiber composites were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, and total reflectance Fourier transform infrared spectroscopy. The results indicated that lignophenol uniformly adhered to the pulp fibers but no chemical bonding occurred. Additionally, both virgin and recycled softwood pulp fiber sheets (80 g/m$^2$) were tested using the same method. Although the strength of all composites increased after impregnation, the most obvious improvement was observed in the hardwood pulp-based composite. This simple method improved the physical strength and hydrophobicity of the composite sheets.

*Keywords: Lignophenol; Pulp fibers; Physical properties; Interaction*

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## INTRODUCTION

Lignin is an amorphous aromatic polymer and an extremely important renewable biomass resource. The lignin from plant cell walls is used as an adhesive to consolidate and support hemicellulose and cellulose (Chen *et al.* 2017). Lignin is sensitive to light and heat and can be degraded by chemical and mechanical interactions. Hence, its structure can be severely damaged during the pulping process. For this reason, lignins have not been industrially applied on a large scale (Mancera *et al.* 2011).

To optimize the functional groups and application of lignin, Funaoka and Abe (1989) developed a phase separation method by which native lignins can be converted into lignophenols by treatment with organic solvents (*p*-cresol) and acid solutions. The lignophenol derivatives have a linear structure, low molecular weight, and high solvent solubility (Nagamatsu and Funaoka 2003; Funaoka 2013). These materials were used in the authors' previous study, in which an impregnation method was used to create lignophenol-pulp fiber sheet composites (Dai *et al*. 2015).

In this study the relationship between the amount of absorbed lignophenol and the mechanical strength of paper sheet composites was investigated by analyzing the fiber morphology (length, width, and degree of polymerization) and adjusting the effect of the

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concentration of the lignophenol acetone solution. In addition, the morphology, chemical composition, and molecular interactions between the lignophenol and pulp fiber sheets were characterized *via* scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The authors expect these results to provide useful reference data for the development of lignophenols for composite applications.

## EXPERIMENTAL

### Materials

The hardwood and softwood pulps of bleached *Eucalyptus* kraft pulp and Botnia Rauma90 kraft pulp, respectively, were obtained from the UPM-Kymmene Corporation (Changshu Mill, China). The waste paper pulp was collected from the core layer of waste Tetra Pak® (Yili pure milk box), and the plastics and non fibrous materials were peeled off. All of the pulps had the same beating degree of 18 °SR. A 60-mesh extractive-free bamboo meal (8.12% moisture, 26.43% lignin) was used to prepare the lignophenols with a two-step phase separation method (Funaoka *et al.* 1989, 1998; Dai *et al.* 2015). The authors then used the resulting lignophenol products to prepare lignophenol-acetone solutions with concentrations of 10 g/L, 30 g/L, 50 g/L, 80 g/L, and 105 g/L at uniform temperature and pressure conditions. The reagent grade acetone was supplied by Sinopharm Chemical Reagent Co. Ltd., China.

### Methods

*Degree of polymerization and fiber morphology*

The degrees of polymerization of the hardwood, softwood, and waste pulps were measured according to the Chinese GB/T 1548-1989 (1989) standard. The basic morphology of the fibers, including the length, width, and aspect ratio, were measured using a Mesto Fiber Lab instrument (Metso Corporation, Helsinki, Finland).

*Papermaking and characterization of physical properties*

The three pulps were used to make 80 g/m$^2$ paper under uniform conditions. First, the pulps were immersed in lignophenol-acetone solutions (concentration 80 g/L) of different concentrations for 12 h. After immersion, the papers were removed from the acetone solution and air-dried to a constant weight to remove the organic solvent and obtain the lignophenol-pulp sheet composites. The moisture content of the lignophenol impregnated paper sheets and un-impregnated control samples was adjusted *via* heat treatment at a constant temperature for 4 h. Next, the tightness (GB/T 451.3 (2002)), tensile strength (ISO 1924-2 (1994)), tear strength (ISO 1974 (1990)), and burst degree (ISO 2758 (2001)) were measured according to their respective standards, as well as other physical properties of the papers. The tightness was measured by thickness meter (YIBIN paper making mill, China). Tensile strength was measured by WZL-300 Paper tensiometer (Hangzhou Qingtong Instrument Development Co. LTD); tearing strength was measured by J-SLY1000A Paper Tearing Tester (Sichuan Changjiang Paper Equipment  Co. LTD).

*Paper morphology and fiber-lignin interaction*

A thermal field emission SEM (JEOL JSM-7600F operated at a voltage of 30 Kv, JEOL Ltd., Tokyo, Japan) was used to observe the microscopic morphology of the

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lignophenol-paper composites. The XPS (Shimadzu Axis Ultra DLD, Tokyo, Japan) was used to analyze the changes in the carbon and oxygen content before and after the preparation of the composite. The X-ray source was monochrome A-l K-α, operated at 15 kV and 15 mA. An ATR-FTIR (VERTEX80V, Bruker, Germany) analysis was performed to examine the chemical bonding between the lignophenol and paper fiber.

## RESULTS AND DISCUSSION

### Effect of Lignophenol Acetone Solution Concentration on Composite Properties

The physical properties before and after adding lignophenols are shown in Table 1. This data indicated that an increase in the concentration of lignophenol acetone solutions resulted in an increased amount of absorbed lignophenol on the paper and improvement of the physical properties. When the solution concentration was 80 g/L, the physical properties of the paper composite were optimal. When the solution concentration exceeded 80 g/L, the amount of adsorbed lignophenol continued to increase and the tear index and burst index began to decline. These findings indicated that an increased amount of dispersed lignophenol in the spaces between the fibers resulted in gradual saturation, causing the degradation of several physical properties of the paper (Gao 2006).

**Table 1.** Changes of Physical Properties of Hardwood Pulp with Different Concentrations of Lignophenol Acetone Solution

| Concentration (g/L) | Absorption Amount (%) | Tightness (%) | Tensile Index (%) | Tearing Index (%) | Bursting Index (%) |
|---|---|---|---|---|---|
| 10 | 12.00±1.00 | -5.88±0.10 | 57.80±2.30 | 56.33±0.70 | 67.82±1.80 |
| 30 | 15.00±0.50 | -5.88±0.10 | 116.67±3.20 | 0.41±0.10 | 73.56±1.30 |
| 50 | 18.00±1.10 | -3.92±0.20 | 121.60±1.10 | 8.99±1.30 | 77.01±2.40 |
| 80 | 21.00±0.80 | 5.66±0.10 | 160.08±3.50 | 93.66±1.50 | 140.00±2.20 |
| 105 | 23.00±1.10 | 7.55±0.20 | 165.33±1.60 | 91.79±1.30 | 137.50±1.60 |

### Analysis of the Properties of Lignophenol-hardwood Pulp

An SEM micrograph of the fiber morphology of the composite paper is shown in Fig. 1a (3000× magnification), where a uniform dispersion of the lignophenol on the fibers is evident. There was a distinct difference between the morphology of the impregnated sample and that of the untreated fiber, which showed a smooth surface (Fig. 1b). As shown in Fig. 1, the interfacial compatibility between the filler (lignophenol) and the matrix phase (fiber) in this kind of polymer composite was good. In addition, it was clear that the particle size of the lignophenol was small enough to allow it to pass through the fiber gap during solvent permeation (by either physical or chemical interactions) and adsorb onto the surfaces of the fiber. In this case, lignophenol worked as a filler in the cellulose fiber matrix phase, which played an enhanced role. These results are consistent with previous findings that showed that the use of lignin polymer-wood fiber composites can improve the internal bonding strength of the composite materials (Naseem *et al.* 2016).
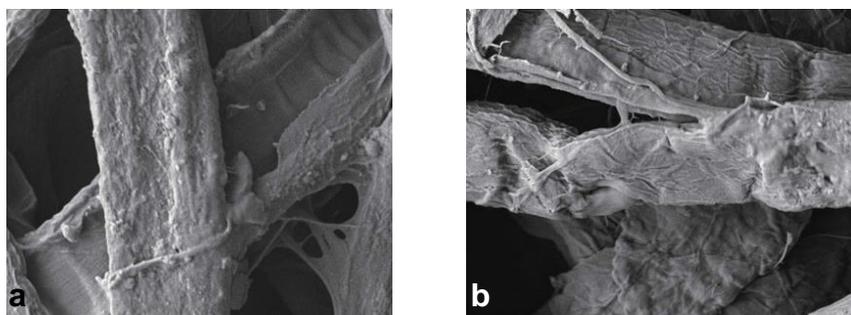
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**Fig. 1.** SEM picture of lignophenol modified paper and unmodified paper; (a) Lignophenol modified hardwood pulp fiber and (b) Hardwood pulp fiber

## Surface Chemistry

XPS has been increasingly used for the surface analysis of fiber and paper (Zhou *et al.* 2015). As hydrogen atoms are not sufficiently sensitive to X-rays, carbon and oxygen atoms are usually the subjects of the XPS analysis of organic materials. The standard electron ability of $O_{1s}$ is detected around 532 eV and the $C_{1S}$ peak is around 285 eV. The $C_{1s}$ peak is actually composed of four smaller peaks, $C_1$, $C_2$, $C_3$, and $C_4$, which appear at binding energies around 285 eV, 286.5 eV, 288.3 eV, and 289.5 eV, respectively (Kalina *et al.* 2014; Migneault *et al.* 2015). The four peaks represent the carbon atoms linked only to C and H, non-carbonyl oxygen atoms, two non-carbonyl oxygen atoms or one carbonyl oxygen, and a carbonyl oxygen and a non-carbonyl oxygen, respectively. The ratio of oxygen to carbon atoms (O/C) in the depth range detected by XPS is related to the lignin content on the fiber surface. As previously reported (Hua *et al.* 1993; Koljonen *et al.* 2003), there exists no single C-C or C-H bonds in cellulose materials. Therefore, the $C_1$ peak appears only in lignin and extractives. Hence, if the C1 peak area was larger, the corresponding peak areas of C2, C3, and C4 were smaller, because oxygen atoms only connect to these types of carbon bonds. Therefore, a higher O/C ratio corresponded to more exposed carbohydrate molecules on the fiber surface. In contrast, a lower O/C ratio was related to a higher content of lignin and extractives on the fiber surface.
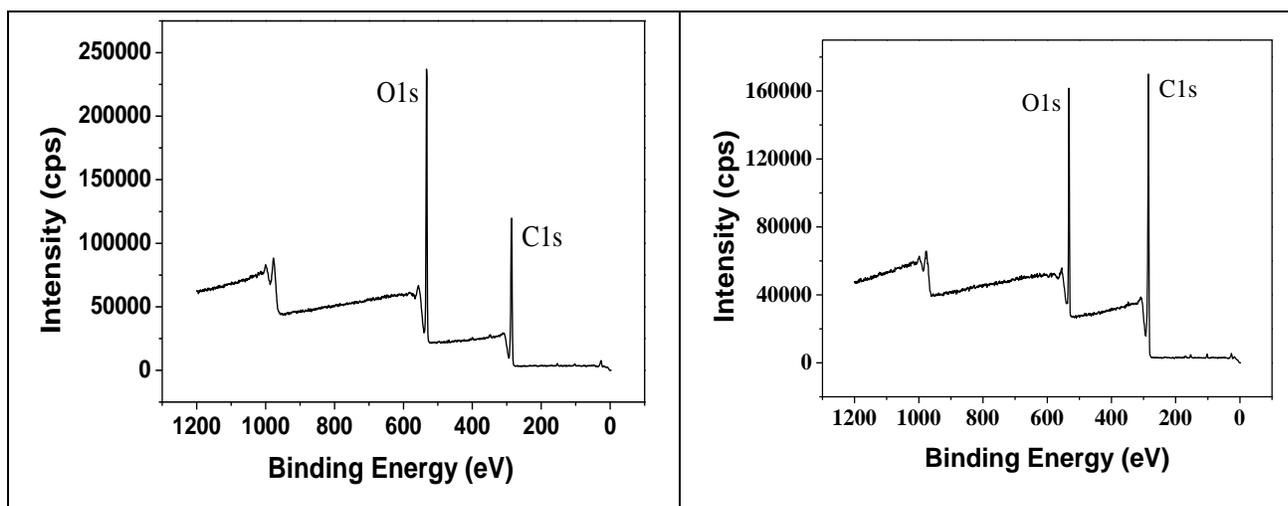


**Fig. 2.** XPS spectra of paper sheet (a) unmodified paper and (b) modified paper

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The main purpose of the XPS study of the hardwood paper and lignophenol-hardwood paper composite was to analyze changes in the distribution of elements on the paper surface using the $C_{1S}$ and $O_{1S}$ peaks and the corresponding O/C ratio. As shown in Fig. 2, only noticeable peaks of carbon and oxygen were identified. Table 2 shows that the O/C ratio of the surface of the hardwood paper composite was noticeably reduced after lignophenol impregnation (from 0.52 to 0.26), which corresponded to an increase in the lignin content on the hardwood paper surface.

**Table 2.** O/C Ratio of Hardwood Paper Sheet and LPS Modified Hardwood Paper Sheet

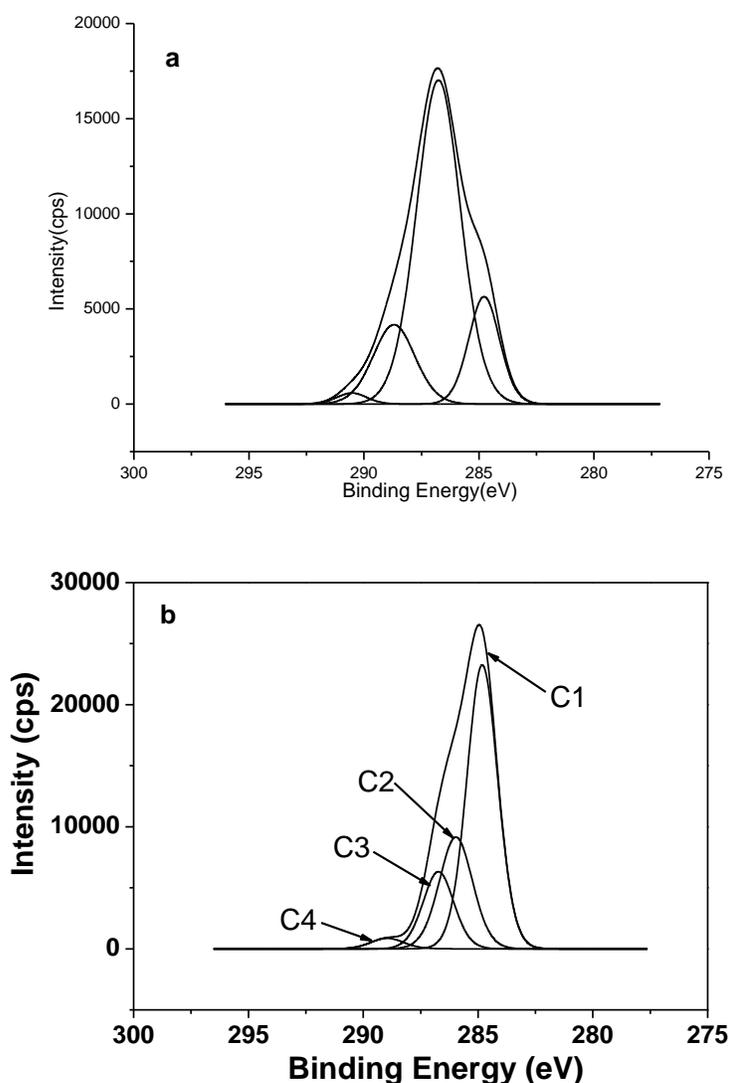| Material | $O_{1S}$ (%) | $C_{1S}$ (%) | O/C |
|---|---|---|---|
| Hardwood Paper | 34.17 | 65.83 | 0.52 |
| Lps Modified Hardwood Paper | 20.64 | 79.36 | 0.26 |



**Fig. 3.** $C_{1s}$ Peak characteristics curve (a) Hardwood paper and (b) Lignophenol-hardwood paper composite

As mentioned above, the $C_1$ peak was mainly related to lignin and extractives, whereas the $C_2$ and $C_3$ peaks were related to carbohydrates. Lignin generally has a higher proportion of the $C_1$ peak. A detailed characterization of the $C_{1s}$ peaks before and after composite preparation is shown in Fig. 3, where the area of the $C_1$ peak increased from 15.6% to 57.6% (an increase of 41.9%). The area of $C_2$ decreased 42.7%, while the peak areas of $C_3$ and $C_4$ did not change. The increase in the $C_1$ peak area was related to an increase in the lignin content due to the lignophenol adsorbed onto the paper surface. In addition, the relative amount of carbohydrates decreased, which was demonstrated by the reduction in the $C_2$ peak area. In summary, by comparing the changes in the carbon valence ratio before and after composite formation, it was further demonstrated that the lignophenols successfully attached to the hardwood pulp, which changed the distribution of the elements and the functional properties of the paper surface.

## Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy Results

The ATR-FTIR spectra of lignophenol, hardwood pulp paper, and lignophenol-hardwood pulp paper composites are shown in Fig. 4. A strong absorption peak at 3390 $cm^{-1}$ was visible in the lignophenol spectrum, which originated from the relatively high amount of hydroxyl groups (Nonaka and Funaoka 2011). In the spectra of the hardwood paper and lignophenol-hardwood paper composite, the absorption peaks related to the stretching vibration of O-H were observed in the range of 3200 $cm^{-1}$ to 3550 $cm^{-1}$. These peaks showed no noticeable changes before and after impregnation of the lignophenol, which indicated that the hydroxyl groups of cellulose did not change due to the attachment of the lignophenol. In addition, no obvious surface chemical bonds were observed for the lignophenol-hardwood paper composite. The enhancement of the physical properties of the paper composite was thought to have been due to the hydrogen bonding between the cellulose and lignophenol. Because the absorbed lignophenols were thought to behave as fillers in the pulp fiber matrix, the interface compatibility was sufficient to increase the strength.
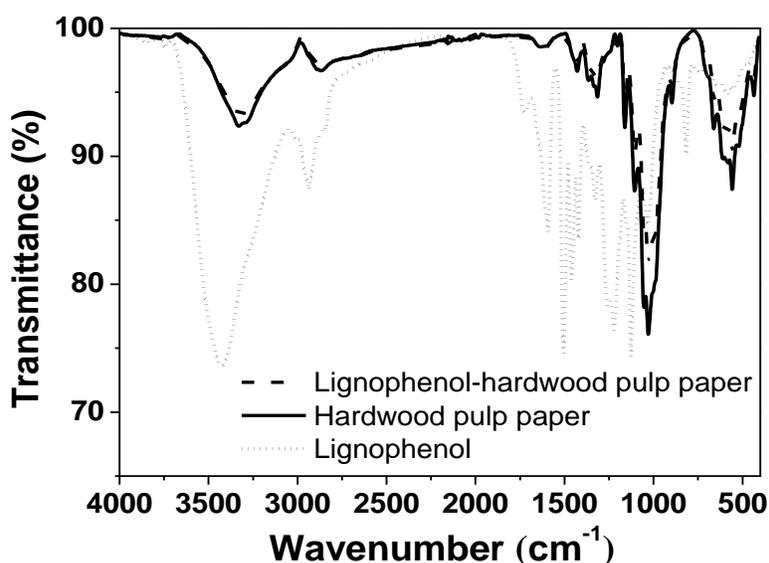


**Fig. 4.** FTIR spectra of modified and unmodified paper sheet

**Effect of Recycled Paper Pulp on Lignophenol Composite Paper**

Recycled paper has a low cost and high availability. As such, its application in paper composites is of great interest. In this study, the Tetra Pak® core layer was tested as a raw material for addition to the lignophenol composite paper. The authors compared the morphologies (length, width, and degree of polymerization) of the recycled fibers with the virgin bleached softwood paper and hardwood paper, and analyzed the effect of the different fiber morphologies on the lignophenol.

**Table 3.** Comparison of Basic Fiber Properties

| Samples | Mean Length (mm) | Mean Width (μm) | Degree of Polymerization (DP) |
|---|---|---|---|
| Recycled Pulp | 1.10±0.02 | 35.80±0.50 | 1360.60±30.00 |
| Softwood Pulp | 2.20±0.14 | 23.60±0.80 | 1143.20±26.00 |
| Hardwood Pulp | 0.75±0.05 | 14.40±1.10 | 1050.60±42.00 |

**Table 4.** Paper Physical Properties Changes before and after 80 g/L Lps Impregnation

| Samples | Porosity ($\varepsilon$) | Absorption Amount (%) | Tightness (%) | Tensile Index (%) | Tearing Index (%) | Bursting Index (%) |
|---|---|---|---|---|---|---|
| Recycled Pulp | 0.64 | 19.25 | 13.56 | 13.83 | -13.72 | 11.44 |
| Softwood Pulp | 0.66 | 19.27 | 16.00 | 75.97 | 52.52 | 34.27 |
| Hardwood Pulp | 0.68 | 21.00 | 5.66 | 160.08 | 91.79 | 137.50 |

The fiber properties of the three different pulps are shown in Table 3. As shown, the softwood pulp fibers were longer and wider than those of the hardwood pulp fibers. The Tetra Pak® core layer pulp fibers originated from softwood pulp (Zhu 2014) and exhibited the shortest and widest fibers (a result of the fibrillation during the recycling process). Using a method published by Kazi *et al.* (2015), the authors measured the differences in the porosities of the three kinds of paper before and after preparation of the composite (Table 4). In general, a lower degree of polymerization was observed for the shorter fibers. The bonding force between the fibers was lower, which resulted in a higher porosity (Wei 2011). When the concentration of lignophenol acetone solution was 80 g/L, the physical properties of the lignophenol-hardwood paper composite were optimal. Therefore, the same concentration was used to make composites with the softwood and recycled pulp papers (80 g/m$^2$). The physical properties of the papers before and after impregnation are shown in Table 4. The improvement in the physical properties of both the softwood and recycled pulp paper composites was less than that observed for the hardwood pulp paper composite. This was because the porosity values of the softwood and recycled papers were lower than that of the hardwood pulp paper and less lignophenol was adsorbed onto the surface. Hence, the relative improvement of the physical properties was smaller (Dai *et al.* 2015). The recycled softwood fiber was wider and shorter due to the fibrillation and compaction of the fibers that occurred during papermaking, which resulted in the lower porosity of the recycled paper compared to the virgin pulp papers.

In summary, the authors demonstrated that the impregnation method of forming lignophenol paper composites could improve paper strength for the three different pulp types tested here. The performance of the composite decreased in the order of hardwood pulp > softwood pulp > recycled softwood fiber.

## CONCLUSIONS

1. It was demonstrated that the physical properties of paper were improved *via* formation of a composite with lignophenol using a simple impregnation method. The use of a lignophenol acetone concentration of 80 g/L resulted in optimum physical properties of the paper composite. There were no identified chemical bonds between the lignophenol and paper fibers by the ATR-FTIR analysis.

2. The SEM and XPS analyses indicated that the addition of lignophenols on the fiber surface enhanced the physical properties of composite paper in a similar manner to the addition of fillers into a polymer matrix.

3. Under the same experimental conditions, softwood and recycled waste paper pulps showed slightly lower improvements in the properties of the papers with the addition of lignophenols compared to hardwood fibers. It was indicated that the morphology of the fiber considerably affected the adsorption and composite behavior. The hardwood pulp showed the greatest promise for an improvement in the physical properties when using this impregnation method to develop lignophenol paper composites.

## ACKNOWLEDGMENTS

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