



Research article

Improvement of paperboard moisture resistance by coating with lignin using the rapid expansion of subcritical solutions process

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Abstract

The rapid expansion of subcritical solutions (RESS) process was successfully carried out to coat paperboard with lignin to improve its moisture barrier property. This work focused on systematic study of effects of the RESS conditions—lignin concentration, pre-expansion temperature and pressure (T_{pre} , P_{pre} , respectively)—on the surface morphology, surface roughness and moisture barrier properties of lignin-coated paperboard. Fourier transform-infrared spectroscopic analysis was performed to ensure the presence of the lignin coating layer on the substrate surface. Typically, the coating layer on the paperboard surface consisted of submicron lignin particles and thin films. The presence of discrete submicron particles decreased when the concentration of lignin was reduced from 0.50% to 0.25% and when the pre-expansion temperature was increased from 80°C to 100°C. The air leakage and water vapor transmission rates of lignin-coated paperboard were primarily controlled by the presence of the uniform coating layer and the thin film of lignin, respectively. The moisture barrier property of paperboard increased after coating with lignin. Among the tested operating conditions, the RESS coating of 0.50% lignin solution at $T_{pre} = 100^\circ\text{C}$ and $P_{pre} = 13.8\text{ MPa}$ effectively provided a smoother and more uniform continuous coating layer on the paperboard surface with up to 20% improved moisture resistance.

Introduction

Lignin, the second most abundant naturally occurring polymer next to cellulose, is the byproduct of paper pulp production (black liquor) with low added-value and limited applications (Hult et al., 2013a). Lignin is generally an amorphous

polyphenolic macromolecule and is composed of a large number of polar functional groups, with the main precursors of lignin being three monomers (phenylpropanoids) derived from *p*-coumaryl, coniferyl and sinapyl alcohols (Gordobil et al., 2015). Nowadays, lignin can be used as a coating agent in many applications. For example, lignin-containing polymer composites produced plastic films with improved water resistance and gas barrier properties (Hult et al., 2013a, 2013b)

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E-mail address: amporn.s@ku.ac.th (A. Sane)online 2452-316X print 2468-1458/Copyright © 2021. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>), production and hosting by Kasetsart University of Research and Development Institute on behalf of Kasetsart University.<https://doi.org/10.34044/j.anres.2021.55.3.11>

and coating with lignin enhanced the film forming properties (Mulder et al., 2011).

Paper plays an important role in the packaging industry, with approximately 35% being used for packaging applications, such as paper bags, folding cartons and wrapping paper (Andersson, 2008). Paper material is produced by the entanglement and compression of cellulose fibers and even though such products have numerous advantages including recyclability, biodegradability and flexibility, there are some limitations, such as weakness in a high moisture environment and low barrier properties (Andersson, 2008). The surface properties of paper are primarily dependent on the surface structure and can be altered by surface modification. In conventional coating techniques, coating substances are applied directly on the substrate surface to create a coating layer and this is often used in the packaging industry due to its easy process and the flexibility of the coating substrates (Wicks et al., 2007). There are several conventional coating methods such as blade coating, surface sizing, film coating, spray coating and curtain coating (Paltakari, 2009). Mostly, these coating methods provide microscale surface roughness and the mixture of coating substances usually consists of particles or pigments, binders, volatile compounds and additives (Tracton, 2006). Coating substances generally interact with the substrate by bonding between the binder and substrate and between particles and the substrate (Tracton, 2006).

Rapid expansion of sub- or supercritical solutions, the so-called RESS process uses high pressure to produce nano- to micron-sized particles. In this process, a pressurized solution containing a solute and a solvent (typically a mixture of supercritical carbon dioxide and an organic solvent) is rapidly (1×10^{-6} s) expanded across a micro-orifice, causing a sudden decrease in solvent density and, hence, a dramatic increase in the solution degree of saturation, leading to precipitation of the solute in the form of fine particles (Tom and Debenedetti, 1991; Blasig et al., 2002). The RESS process has been used to produce ultrafine particles from a variety of substances, including organic, polymeric and inorganic materials. Several research groups have investigated the effect of RESS processing conditions including the solute concentration, pre-expansion temperature and pressure (T_{pre} and P_{pre} , respectively), nozzle geometry and spraying distance on the product size and morphology (Tom and Debenedetti, 1991; Blasig et al., 2002; Sodeifian et al., 2019). Recently, RESS with solid cosolvent has been reported to produce drug nanoparticles from letrozole, aprepitant and coumarin-7 dye (Sodeifian and Sajadian, 2018; Sodeifian et al., 2018). RESS has also been extended to coating applications (Chernyak et al., 2001; Fulton et al., 2003;

Ratcharak and Sane, 2014). RESS coating has advantages over conventional coating technique including providing ultrafine particles which subsequently form a thin coating layer on the substrate surface and facilitating the removal of a solvent by the rapid expansion of supercritical carbon dioxide (Tom and Debenedetti, 1991; Chernyak et al., 2001).

RESS coating has been investigated for coating fluoropolymers onto biodegradable material (Ratcharak and Sane, 2014) and metal substrates (Fulton et al., 2003). To date, there has been no report on applying RESS for coating lignin onto paperboard. The current study systematically investigated the potential of the RESS process to coat paperboard with lignin and the effects of the RESS conditions, namely the lignin concentration and the pre-expansion temperature and pressure (T_{pre} , P_{pre} , respectively) on the surface morphology, surface roughness and moisture barrier properties of lignin-coated paperboard.

Materials and Methods

Materials

Lignin extracted from black liquor using precipitation of the liquefied-lignin fractions was kindly supplied by Clemson University (Velez and Thies, 2013). Paperboard (Duplex board 300 g/m²) was obtained from Thai Union Paper Industry (Thailand) and used as a substrate for lignin coating. Carbon dioxide (CO₂, $\geq 99.98\%$ purity) was obtained from Chattakorn Lab Center (Thailand). Ethanol (99.9% purity) was purchased from Merck (Germany).

Measurements of phase behaviors of lignin subcritical solutions

A schematic diagram of the apparatus used to investigate the phase behaviors of lignin solution is shown in Fig. 1. Experimentally, a variable-volume view cell was charged with 5.00 g of lignin solution in ethanol (0.50% and 1.00% lignin) and 5.00 g of CO₂. The view cell was placed inside an isothermal bath and the mixture was heated to approximately 90–100°C and then pressurized to 34.0 MPa, using CO₂ from a syringe pump, under continuous stirring with a horseshoe magnet until a homogeneous solution was obtained. To determine the cloud-point pressure (liquid to liquid-liquid phase transition), the pressure in the view cell was slowly decreased (at approximately 2.5 bar/min) until the clear solution became slightly hazy. After the cell temperature reached 90–100°C, the heating was stopped and the cloud-point pressures were determined as the solution slowly cooled down (approximately 0.1°C/min) to room temperature.

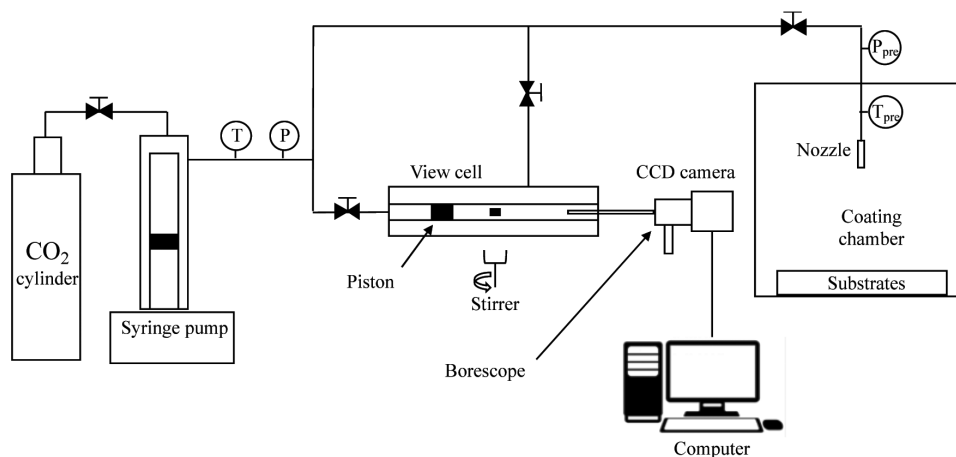


Fig. 1 Schematic of the phase behavior and apparatus for rapid expansion of subcritical solutions

Coating paperboard with lignin by rapid expansion of subcritical solutions process

To prepare paperboard coated with lignin, rapid expansion experiments were performed by expanding lignin solutions (0.25% and 0.50%) in a subcritical mixture of CO₂ and ethanol (1:1) across a nozzle (50 μm diameter, length/diameter = 4) into air at ambient conditions (Fig. 1). Initially, a view cell was loaded with a solution of lignin in ethanol and CO₂ in the same manner as described above. After the mixture was compressed to a desired pressure, the cell was heated to 65–70°C under continuous stirring until the clear solution was obtained. Before expanding the lignin solution, steady-state conditions of rapid expansion were established by flowing pure CO₂ under heating from the syringe pump, bypassing the high-pressure cell, to the nozzle in order to obtain constant pre-expansion temperature and pressure (T_{pre} , P_{pre} , respectively) upstream of the nozzle (Fig. 1). Then, the flow of pure CO₂ was redirected to the cell to indirectly push the lignin subcritical solution out of the cell by means of the movable piston located inside the cell. Subsequently, the lignin solution was expanded through the nozzle into air in the coating chamber. The precipitates were deposited onto the paperboard surface located 22 cm from the nozzle outlet (see Fig. 1). All rapid expansion experiments were carried out in duplicate and the coated paperboards were conditioned at 27 $\pm$ 1°C and relative humidity (RH) of 65 $\pm$ 2% for 24 hr before characterization.

Characterization

Attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectroscopic analysis was performed with a dried lignin-coated sample to ensure the presence of the lignin

coating layer on the substrates using a Bruker spectrometer (Tensor 27; Bruker; USA) over a wavenumber range of 4,000–400 cm^{-1} with 32 scans at a resolution of 4 cm^{-1} .

The surface morphology of the paperboard surface after coating with lignin was examined using a scanning electron microscope (SEM; FEI Quanta 450; USA) at an accelerating voltage of 20 kV. All the samples were sputter-coated with gold prior to SEM analysis. Additionally, the surface roughness of the lignin-coated samples was determined using a Bendtsen roughness tester (TMI 58–27; New Castle; USA) and the air leakage method to measure the air leakage rate between the lignin-coated paperboard and the flat surface of a glass plate (Pino, 2011).

The thermal properties of the lignin were determined using a differential scanning calorimeter (DSC1 STARe; Mettler-Toledo; Switzerland) according to the testing method reported by Gordobil et al. (2015). The samples were heated from -80°C to 250°C at a heating rate of 10°C/min and then cooled to -80°C at a rate of 10°C/min under N₂ atmosphere with a flow rate of 10 mL/min.

The water vapor transmission rate (WVTR) of paperboard after coating with lignin was measured using a modification of ASTM Standard E96 (1995) procedure. The measurements were carried out at 37 $\pm$ 1°C and 80 $\pm$ 2% RH.

Data analysis

All results were expressed as Means $\pm$ SD ($n = 3$). The data were analyzed using one-way analysis of variance. Then differences among mean values obtained from various coating conditions were determined using Duncan's multiple range test. The analyses were performed using the SPSS software package (version 10; USA). The tests were considered significant at $p < 0.05$.

Results and Discussion

Phase behaviors of lignin solutions

Concentrations of 0.25% and 0.50% lignin in a mixture of CO₂ and ethanol (1:1) were chosen for the cloud-point measurements. The cloud-point pressures for lignin solutions were measured over a range of 28–100°C and are shown as a pressure-temperature diagram in Fig. 2. The cloud-point pressure of the 0.25% lignin solution increased from 13.1 MPa to 23.5 MPa when the solution temperature increased from 28°C to 88°C. All the cloud-point curves had typical lower critical solution temperature behavior (Blasig et al., 2002; Sane and Limtrakul, 2011), with the cloud-point slopes up to approximately 0.26 MPa/°C. During cloud-point transition, the lignin homogeneous liquid solution (L) was separated into two liquid phases: solvent-rich and solute-rich (L₁L₂). The pressures of cloud-point curve increased by approximately 1.6 MPa when the lignin concentration increased from 0.25% to 0.50%.

Coating paperboard with lignin by rapid expansion of subcritical solutions process

The conditions for spray coating onto the paperboard substrate were selected to ensure that the pre-expansion temperature was above the boiling point of ethanol to avoid its condensation during rapid expansion. In addition, to avoid nozzle clogging due to the solidification of lignin precipitates with the decreasing temperature during rapid expansion, the glass-transition temperature of lignin was determined using a differential scanning calorimeter. The glass-transition temperature of lignin occurred at 60°C (Fig. 3), in agreement with the result reported by Gordobil et al. (2015). Consequently, the pre-expansion temperatures used for RESS coating were chosen above both the boiling point of ethanol and the glass-transition temperature of lignin and were varied in the range 80–100°C for the rapid expansion experiments. In addition, the pre-expansion pressures were varied in the range 13.8–24.2 MPa so that the phase states of the lignin subcritical solutions started from the one- and two-liquid phase regions. The operating conditions for the RESS process were lignin concentrations of 0.25% and 0.50%, T_{pre} in the range 80–100°C and P_{pre} in the range 13.8–24.2 MPa. Fig. 2 shows the selected pre-expansion conditions in relation to the cloud-point curves for the 0.25% and 0.50% lignin solutions.

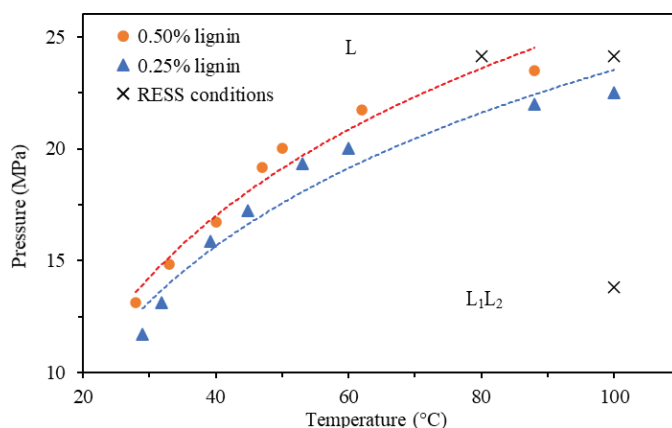


Fig. 2 Cloud-point curves for 0.25% and 0.50% lignin solutions in subcritical mixture of CO₂ + ethanol (1:1) and experimental conditions for rapid expansion of subcritical solutions (RESS) for lignin coatings in relation to their relevant cloud-point curves, where L = lignin homogeneous liquid solution and L₁L₂ = solvent-rich and solute-rich phases

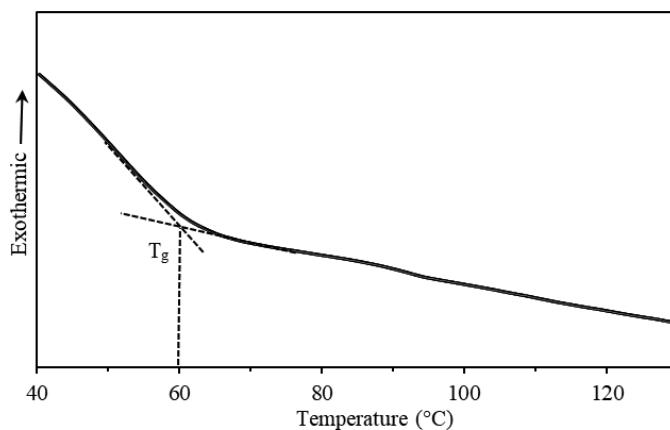


Fig. 3 Differential scanning calorimeter thermogram of lignin, where T_g = glass transition temperature

Scanning electron microscopy

The surface morphology of the paperboard samples before and after coating with lignin was characterized under a scanning electron microscope. Fig. 4 illustrates that the substrates were covered with a thin film and individual submicron particles. Fig. 4A shows that the initial paperboard had a porous surface structure. Following coating with 0.25% lignin at $T_{pre} = 80^\circ\text{C}$ and $P_{pre} = 24.2$ MPa (Fig. 4B), with these conditions being above the cloud-point curve, generally resulted in the formation of a thin film with few submicron particles (approximately 0.4–0.5 μm) coating the surface of the paperboard because the precipitation had started from a homogeneous solution (Blasig et al., 2002). At $T_{pre} = 100^\circ\text{C}$, the size of lignin particles increased to approximately 0.7–1.0 μm and more submicron particles were dispersed on the paperboard surface (Fig. 4C). This could be explained by the rapid expansion at T_{pre} (100°C) above the glass-

transition temperature of lignin (60°C), resulting in lignin droplets with higher temperature and hence an increase in the coalescence of the lignin-rich phase into larger droplets (Blasig et al., 2002; Ratcharak and Sane, 2014). It was also observed that the surface area of the paperboard covered with the lignin film increased (see insert in Fig. 4C). At constant $T_{pre} = 100^{\circ}\text{C}$, decreasing P_{pre} from 24.2 MPa to 13.8 MPa led to larger surface area of paperboard being covered by the lignin coating layer (Fig. 4D), possibly caused by the early precipitation of the lignin subcritical solution at the higher T_{pre} leading to coalescence of the lignin-rich phase into larger droplets which subsequently spread and formed a larger thin film on the substrate surface (Blasig et al., 2002; Ratcharak and Sane, 2014). At the higher concentration of lignin (0.50%), the RESS coating experiments were performed at conditions both above the 0.50% lignin cloud-point curve ($T_{pre} = 80^{\circ}\text{C}$, $P_{pre} = 24.2$ MPa) and below the cloud-point curve ($T_{pre} = 100^{\circ}\text{C}$, $P_{pre} = 24.2$ MPa; $T_{pre} = 100^{\circ}\text{C}$, $P_{pre} = 13.8$ MPa), as illustrated in Fig. 2. For RESS with the pre-expansion conditions of (i) $T_{pre} = 80^{\circ}\text{C}$, $P_{pre} = 24.2$ MPa and (ii) $T_{pre} = 100^{\circ}\text{C}$, $P_{pre} = 24.2$ MPa,

increasing the lignin concentration from 0.25% to 0.50% led to more and larger particles dispersed on the paperboard surface and a larger area of substrate being covered by the lignin film (compare Fig. 4B to Fig. 4E and Fig. 4C to Fig. 4F). However, the presence of submicron particles was substantially reduced and there was more of the thin film of lignin coated on the surface of paperboard when RESS with 0.50% lignin was performed with $T_{pre} = 100^{\circ}\text{C}$, $P_{pre} = 13.8$ MPa (Fig. 4G). The results suggested that during rapid expansion at lower T_{pre} or higher P_{pre} , precipitation of the lignin solution into liquid droplets of the lignin-rich phase occurs and these droplets coalesce to form submicron particles that are deposited on the substrate surface (Ratcharak and Sane, 2014). In addition, the coalesced droplets tend to easily deform and spread to produce a thin film coating on the paperboard when RESS is carried out at higher T_{pre} and lower P_{pre} , which could minimize the cooling effect during the rapid expansion process. Among all the operating conditions, coating with 0.50% lignin solution using $T_{pre} = 100^{\circ}\text{C}$ and $P_{pre} = 13.8$ MPa provided the most uniform coating layer of lignin (compare Fig. 4G and Fig. 4B–F).

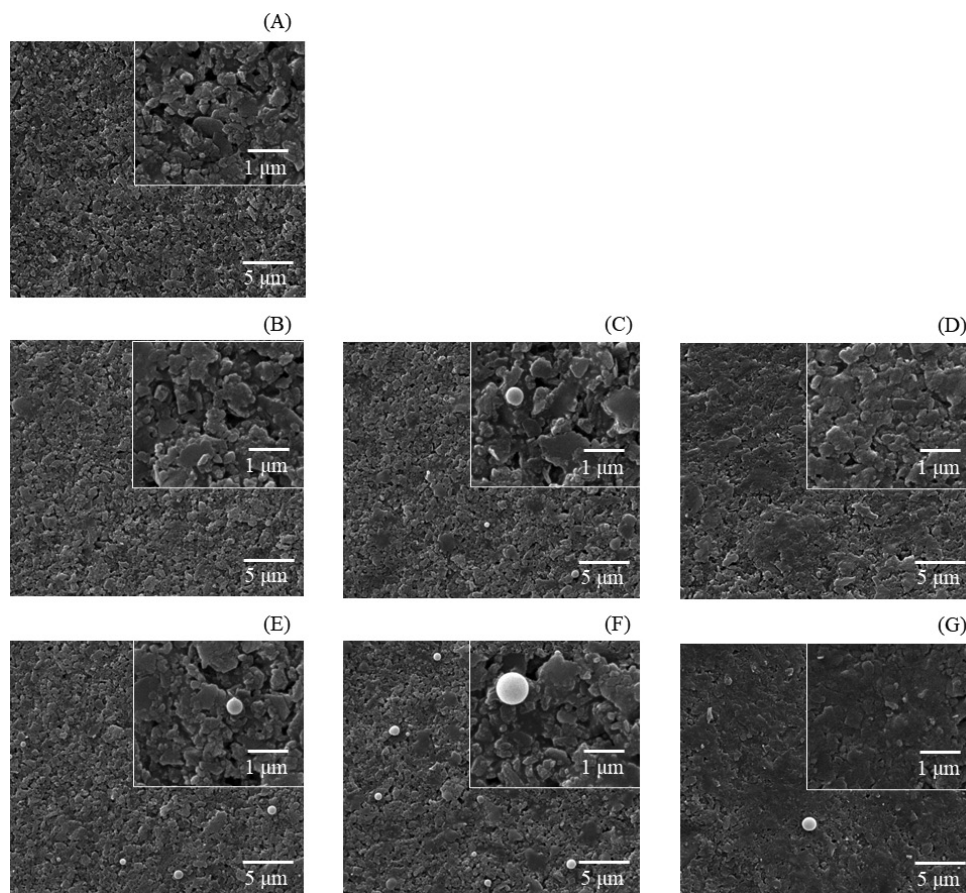


Fig. 4 Scanning electron microscope images with different values for lignin content in the coating, pre-expansion temperature (T_{pre}) and pre-expansion pressure (P_{pre}): (A) uncoated paperboard; (B) 0.25% lignin, $T_{pre} = 80^{\circ}\text{C}$, $P_{pre} = 24.2$ MPa; (C) 0.25% lignin, $T_{pre} = 100^{\circ}\text{C}$, $P_{pre} = 24.2$ MPa; (D) 0.25% lignin, $T_{pre} = 100^{\circ}\text{C}$, $P_{pre} = 13.8$ MPa; (E) 0.50% lignin, $T_{pre} = 80^{\circ}\text{C}$, $P_{pre} = 24.2$ MPa; (F) 0.50% lignin, $T_{pre} = 100^{\circ}\text{C}$, $P_{pre} = 24.2$ MPa; (G) 0.50% lignin, $T_{pre} = 100^{\circ}\text{C}$, $P_{pre} = 13.8$ MPa

Fourier transform infrared spectroscopy

ATR-FTIR characterization was performed for both the initial lignin and the lignin-coated paperboard to ensure the existence of a lignin coating layer on the paperboard surface. However, the spectra of the paperboard interfered with those of lignin. Consequently, the presence of the lignin coating layer was confirmed by coating lignin onto tinplate instead (Fig. 5). The characteristic bands located at wavenumbers $1,429\text{ cm}^{-1}$, $1,464\text{ cm}^{-1}$, $1,509\text{ cm}^{-1}$ and $1,601\text{ cm}^{-1}$ corresponding to the aromatic rings and C-H bonds of initial lignin (Liu et al., 2008; Gordobil et al., 2014) also appeared for the lignin-coated tinplate, confirming the presence of lignin on the solid substrate.

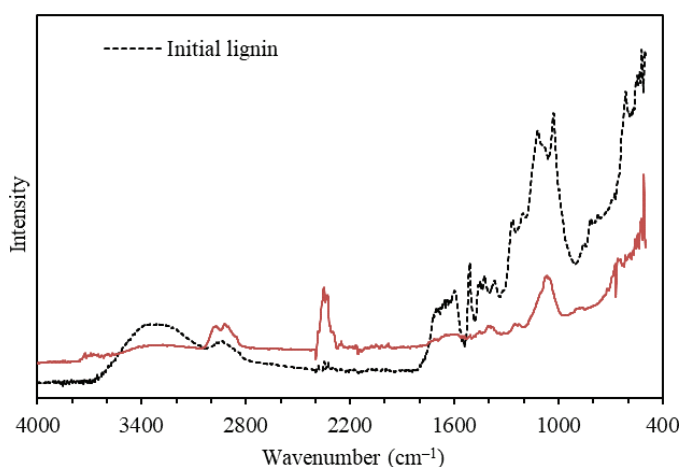


Fig. 5 Fourier transform infrared spectra of initial lignin and lignin-coated tinplate obtained from rapid expansion of subcritical solutions of 0.50% lignin at pre-expansion temperature = 100°C and pre-expansion pressure = 13.8 MPa

Air leakage rate

The results obtained from air leakage testing showed that coating with lignin reduced the rate of air leakage of paperboard from 42.88 mL/m^2 to $29.88\text{--}35.13\text{ mL/m}^2$ (Table 1). The results suggested that coating with lignin using the RESS process reduced the surface roughness of the paperboard. Coating with 0.25% lignin at (i) $T_{\text{pre}} = 80^{\circ}\text{C}$ and $P_{\text{pre}} = 24.2\text{ MPa}$ or (ii) $T_{\text{pre}} = 100^{\circ}\text{C}$ and $P_{\text{pre}} = 13.8\text{ MPa}$ led to lower rates of air leakage, compared to coating with $T_{\text{pre}} = 100^{\circ}\text{C}$ and $P_{\text{pre}} = 24.2\text{ MPa}$. This could be explained by the observed morphology of the coating layer and surface coverage obtained from the different rapid expansion conditions. Expansion of the 0.25% lignin solution at conditions with low T_{pre} (80°C) and high P_{pre} (24.2 MPa), or pre-expansion conditions well above the cloud-point curve (see Fig. 2), resulted in the formation of tiny droplets of the lignin-rich phase uniformly deposited as a thin film in the

background of the paperboard surface (Fig. 4B). When RESS was performed with high T_{pre} (100°C) and low P_{pre} (13.8 MPa), or under pre-expansion conditions well below the cloud-point curve (Fig. 2), the lignin subcritical solution was already phase-separated into larger lignin-rich droplets at the higher temperature and subsequently, the droplets deformed and spread on the surface of the paperboard, leading to more formation of lignin coating layer (see insert in Fig. 4D). However, when coating was performed with high T_{pre} (100°C) and P_{pre} (24.2 MPa), or under pre-expansion conditions just above the cloud-point curve of 0.25% lignin (Fig. 2), a higher rate of air leakage of coated samples was obtained, possibly because the lignin-rich phase remained as precipitated droplets upon depositing on the substrate and provided less surface coverage (compare inserts in Fig. 4C and Fig. 4D) due to the cooling effect during rapid expansion of the CO_2 solution from the higher pressure. The SEM results in Fig. 4 confirmed that increasing the lignin concentration from 0.25% to 0.50% during RESS coating led to the formation of more discrete particles distributed on the surface of the substrates (Fig. 4E–4G). Accordingly, these results suggested that the presence of the discrete particles of lignin had no significant effect on the air leakage rate of the coated paperboard. Furthermore, increasing the lignin concentration did not substantially affect the surface roughness of the paperboard. The surface roughness of the coated samples was reduced in the RESS experiments with 0.25% and 0.50% lignin were carried out with (i) low T_{pre} (80°C) and high P_{pre} (24.2 MPa) and (ii) high T_{pre} (100°C) and low P_{pre} (13.8 MPa), as these conditions provided a uniform coating layer of lignin as observed in the SEM analysis (Fig. 4B, 4E, 4F and 4G).

Water vapor transmission rate

The results obtained from the WVTR measurements illustrated that coating with lignin reduced the WVTR of paperboard from $504.00\text{ g/m}^2\cdot\text{d}$ to $410.67\text{--}489.79\text{ g/m}^2\cdot\text{d}$ (Table 1), in agreement with the results obtained from air leakage testing. The results suggested that coating with lignin using the RESS process improved the moisture barrier property of paperboard up to approximately 20%. The WVTR values of the lignin-coated paperboard samples depended on the rapid expansion conditions which determined the morphology of the lignin coating layer. The WVTR was primarily controlled by the presence of the thin film of the lignin coating layer instead of by the discrete submicron particles. The lowest WVTR of $410.67\text{ g/m}^2\cdot\text{d}$ (Table 1) was obtained from the paperboard coated using RESS and 0.50% lignin at $T_{\text{pre}} = 100^{\circ}\text{C}$ and $P_{\text{pre}} = 13.8\text{ MPa}$, due to the presence of the thin lignin film in the coating layer (Fig. 4G).

Table 1 Air leakage rate and water vapor transmission rate of paperboard coated with lignin at different concentrations and pre-expansion conditions (T_{pre} , P_{pre})

Lignin concentration (%)	T_{pre} (°C)	P_{pre} (MPa)	Rate of air leakage (mL/m ²)	WVTR (g/m ² d)
0	-	-	42.88±1.81 ^c	504.00±23.70 ^d
0.25	80	24.2	30.25±3.85 ^a	460.52±28.74 ^{bc}
	100	24.2	33.00±2.39 ^{ab}	489.79±11.58 ^{cd}
	100	13.8	32.63±2.07 ^{ab}	478.97±23.52 ^{cd}
0.50	80	24.2	29.88±3.23 ^a	431.03±21.30 ^{ab}
	100	24.2	35.13±1.89 ^b	480.67±26.15 ^{cd}
	100	13.8	31.63±3.29 ^a	410.67±32.09 ^a

T_{pre} = pre-expansion temperature pressure; P_{pre} = pre-expansion pressure; WVTR = water vapor transmission rate

Mean±SD in a column superscripted with different lowercase letters indicate significant ($p < 0.05$) differences.

In summary, the current study showed the capacity of the RESS process for coating paperboard with lignin. During the rapid expansion process, lignin was precipitated from subcritical solutions and coated on the paperboard surface. In general, the coating layer consisted of submicron particles and thin films of lignin. The presence of discrete particles reduced when the lignin concentration decreased from 0.50% to 0.25% and the pre-expansion temperature increased from 80°C to 100°C. The air leakage and water vapor transmission rates of the lignin-coated paperboard were generally determined by the presence of the uniform coating layer of lignin. The moisture barrier property of the paperboard increased (up to approximately 20%) after coating with lignin. The highest moisture resistance was obtained when RESS coating was performed with 0.50% lignin solution at $T_{pre} = 100^\circ\text{C}$ and $P_{pre} = 13.8$ MPa. Finally, RESS should be a promising process for lignin coating to improve the moisture resistance of paperboard.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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