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Application of Polyvinyl Acetate/Lignin Copolymer as Bio-Based Coating Material and Its Effects on Paper Properties

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Abstract: In this work, lignin-vinyl acetate copolymers containing different fractions of lignin were synthesized by the copolymerization technique. The synthesized copolymer was successfully applied to coat the paper for enhancing its properties and performance. The effects of the lignin-vinyl acetate copolymer on the physicochemical, air permeability and mechanical properties of paper were investigated. The mechanical strength, hydrophilic, and air permeability properties of coated paper were improved with the increasing content of the lignin. Lignin-vinyl acetate copolymer containing 15% lignin coated paper exhibited a 1.86 times increase in the tensile index, 45 times increase in the water contact angle, and a 41.1% reduction in the air permeability compared with uncoated paper. Scanning electron microscopy was applied to study the morphology of the coated and uncoated paper. The results showed that paper surface porosity structure was decreased, while the surface smoothness was enhanced considerably with increasing lignin fraction in the copolymer. Therefore, the successful fabrication of such an enchanting coated paper may afford new potential and great applications in the packaging paper.

Keywords: lignin-vinyl acetate copolymer; coating paper; physicochemical and mechanical properties

Citation: Zhang, N.; Liu, P.; Yi, Y.; Gibril, M.E.; Wang, S.; Kong, F. Application of Polyvinyl Acetate/Lignin Copolymer as Bio-based Coating Material and Its Effects on Paper Properties. *Coatings* **2021**, *11*, 192. <https://doi.org/10.3390/coatings11020192>

Academic Editors: Csaba Balázs and Jean-François Berret
Received: 14 December 2020
Accepted: 5 February 2021
Published: 7 February 2021

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1. Introduction

Paper is widely used in many industries and day-to-day life as a packaging material due to its unique properties such as flexibility, low cost, sustainability, recyclability, non-toxicity, and biodegradability [1]. However, poor water-resistance and low mechanical properties are the main reasons hindering its applications in wide fields [2]. This is the result of the complex chemical structure of cellulose fibers and their arrangement at different levels, namely at molecules, fibrils, fibers, and fiber mat (paper), which may have the main role in determining many end-uses and the properties of paper [3]. Therefore, there is an urgent demand for improving the physicochemical and mechanical properties.

Coating paper surface is a common technique to enhance the physicochemical and mechanical properties. Currently, different types of polymeric materials, including starch, polyvinyl alcohol (PVA), polyethylene (PE), silicone, and modified polyvinyl acetate (PVAc), have been used intensively in paper coating for enhancing its functional performance [2]. Amongst these polymeric materials, PVAc is a thermoplastic polymer obtained by polymerization of vinyl acetate monomers [4]. PVAc is non-toxic, inexpensive, easy to synthesize, and biodegradable. PVAc has been used widely in different daylife applications such as a raw material for the preparation of polyvinyl alcohol (PVA), adhesive glue for wood and paper, and as a thermosetting adhesive material [5–7]. Nevertheless, the low thermal stability of PVAc might hinder its potential practical applications as coating materials [7]. Consequently, there is considerable demand for enhancing the thermal stability of the PVAc using a facile method and inexpensive material to be more suitable and economical in paper coating [8]. Copolymerization of vinyl acetate (VAc) monomer with various petroleum-based monomers including ethylene, butyl acrylate (BA), vinyl chloride, and

methyl methacrylate monomers has been applied as a common method to enhance some properties of the PVAc polymer [9–13]. Most of these PVAc copolymers are inexpensive, commercially available polymers with many desirable properties. However, there is an urgent need to find sustainable and bio-based monomers to be alternative sources that can be used in copolymerization with vinyl acetate.

Lignin is the third-largest natural macromolecular organic substance [14,15]. It has been classified as a byproduct of the paper industry—most of the generated lignin is burned or discharged, although it has excellent properties such as anti-ultraviolet and anti-microbial [16]. Many studies have shown that lignin can effectively filter ultraviolet (UV) light [17], whereas Tian et al. [18] reported that the addition of lignin nanoparticles into the PVA matrix leads to prepare a composite film with a shield of ultraviolet light (at least 70%). It has been also used to enhance the physical and chemical properties of the PVAc polymer in several studies. For example, lignin was blended with PVAc to enhance or add new properties, such as UV resistance [6], to enhance the mechanical properties [19], and to improve the thermal stability of PVAc [20–22]. Consequently, the blending of PVAc with lignin at the molecular level through copolymerization leads to combine the properties of both, expanding the scope of application of PVAc in paper coating and also the utilization of lignin as biosource for coating materials [23–27]. On this approach, and based on our previous work, we found that the adding of lignin to PVAc via copolymerization showed a significant enhancement of the thermal stability of the PVAc [4], which seemed appropriate to be used for coating the paper due to its chemical structure, low cost, and moderate thermal stability.

In the present study, lignin-vinyl acetate copolymer containing different fractions of lignin was synthesized by copolymerization technique. The synthesized copolymer was successfully applied to coat the paper for enhancing its functional performance. The effects of the lignin-vinyl acetate copolymer on the physicochemical, air permeability, and mechanical properties of the coated paper were investigated. Our study was focused on the effect of lignin, which has a great impact on the application of the coating, water resistance, and air permeability properties and could afford new potential applications in paper packaging.

2. Materials and Methods

2.1. Materials

Sodium lignosulfonate was purchased from Shanghai Xushuo Biotechnology Co., Ltd. (Shanghai, China). Formaldehyde was supplied by Laiyang Kangde Chemical Co., Ltd. (Yantai, China). Acetone was purchased from Yantai Far East Fine Chemical Co., Ltd. (Yantai, China). Filter paper was provided from Fushun Civil Administration Filter Paper Co., Ltd. (Fushun, China). The vinyl chloroacetate (CVAc), vinyl acetate (VAc), diethylenetriamine (DETA), benzyl peroxide (BPO), polyvinyl alcohol (PVA) 1799 were provided from Shanghai McLean Biotechnology Co., Ltd. (Shanghai, China). Isopropanol was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China).

2.2. Methods

2.2.1. Polymer Synthesis

PVAc and lignin-vinyl acetate copolymers were synthesized as described in our previous work [4]. In short, synthesis was done in two-steps; firstly, lignin-vinyl acetate (LVAc) monomer was prepared by simple grafting reaction of chlorovinyl acetate with activated lignin. Secondly, as-prepared LVAc and the acetate (VAc) monomers were polymerized in different ratios for the purpose of obtaining PVAc copolymer containing different fractions of lignin. The synthesized PVAc and its copolymers containing different fractions of lignin were separately dissolved in acetone (10 wt.%) to prepare a coating solution in equal concentrations as shown in Figure 1.

Figure 1. Pictures of (a) the prepared copolymers containing different fractions of lignin, and (b) the coating solutions of polyvinyl acetate (PVAc) and its copolymers.

2.2.2. Paper Coating

The dried filter paper was fixed tightly on the moveable holder which was moving at a constant speed (10 mm/s). The coating process with PVAc and its lignin copolymers was achieved using a sprayer at a constant rate (0.2 mL/min). The coating process was applied to one side of the paper, and the coating quantity was controlled to be 0.0067 g/cm². The coated papers were dried to remove acetone and then placed in standard conditions of room temperature and 50% humidity for one day using constant temperature and humidity test dryer model-DHS-010 (YASHILIN, Beijing, China).

2.3. Characterization

2.3.1. Coating Weight

The coating weight of the samples was measured by subtracting the weight of the papers before and after the coating process. The results were averaged from five replicates and presented as the average $\pm$ the standard deviation.

2.3.2. Thermogravimetric Analysis (TGA)

Samples were tested with a TA thermogravimetric analyzer (TGA Q50, Woodland, CA, USA). The test for the samples was conducted under a nitrogen atmosphere (inert). The samples' weights were 5–15 mg and the heating rate was adjusted at 15 °C·min^{−1}; the test temperatures were from 35 to 800 °C with the gas flow of 40 mL/min nitrogen.

2.3.3. Differential Scanning Calorimetry (DSC)

The samples were analyzed using a NETZSCH STA449 thermal analyzer (NETZSCH-Gerätebau GmbH, Filderstadt, Germany). About 10 mg of each sample was placed in a pan (aluminum-oxide) and heated from −10 °C to 200 °C with a heating rate of 10 °C min^{−1} under nitrogen atmospheres.

2.3.4. Ultraviolet (UV) Spectrophotometry

The dried paper was tested on a solid ultraviolet spectrophotometer (UV-2600, Shimadzu, Japan), with a wavelength range from 200 to 800 nm. External dual detection was used to test the absorption wavelength.

2.3.5. Scanning Electron Microscopy (SEM)

The paperboard specimens were cut into $5 \times 5 \text{ mm}^2$ pieces for viewing the surface texture. The samples test was studied by field emission scanning electron microscope (FE-SEM, Regulus 8820, Tokyo, Japan).

2.3.6. Air Permeability Test

Coated papers were cut into a circular piece of paper with an area of 20 cm^2 , and a gas permeability tester (Deliang Testing Instrument Co., Ltd., Taipei, Taiwan, China) under a pressure of 2500 Pa measured the air permeability.

2.3.7. Water Contact Angle

The contact angle of water on the paper surface was measured with a contact angle analyzer (OCA50, Filderstadt, Germany) after a drop of distilled water about $5 \mu\text{L}$ was placed on the surface of the coated or uncoated paper using a microsyringe. All paper samples ($4 \times 6 \text{ cm}^2$) were stuck on the movable sample stage leveled horizontally before the test.

2.3.8. Fourier Transform Infrared Spectroscopy (FTIR)

The coated paper was tested on Bruker's FTIR spectrometer (VERTEX70 FTIR, Karlsruhe, Germany). Each sample was scanned 32 times with a wavelength range of 400 to 4000 cm^{-1} .

2.3.9. Mechanical Properties

Coated papers were cut into $63 \times 75 \text{ mm}^2$ and tear index measured by a tear tester (SLY-1000, Labthink, Jinan, China). Then, the paper was cut into $15 \times 250 \text{ mm}^2$ and the tensile index was measured by a tensile machine (XWL (B), Labthink). Coated paper with a diameter of more than 5 cm was then selected to test the burst index by burst resistance meter (BSM-1600B, Hangzhou Qingtong Brocade Automation Technology Co., Ltd., Hangzhou, China).

2.3.10. Surface Free Energy Measurement Method

The surface free energy (SFE) for coated papers was determined by measuring the contact angles (θ) between the solid surface (coated papers) and the test liquids, with known surface tensions (water), free surface energies of the coated papers were calculated using automatic Owens, Wendt, Rabel, and Kaelble (OWRK) calculation method [28,29]. The OWRK method is the most frequently used method for the determination of SFE (γ) of polymer surfaces, along with their polar (γ^p) and dispersive (γ^d) part. The liquid was a droplet on the surface with a volume of $1 \mu\text{L}$. The contact angles of the droplet were captured by a high-resolution charge-coupled device (CCD), camera, and measured after the initial contact of the droplet with the surface [30].

3. Results and Discussion

3.1. Scanning Electron Microscope and Water Contact Angle Analysis

To investigate and understand the morphology of the blank and coated paper, the samples were analyzed by the FE-SEM. Figure 2 shows the FE-SEM images of a blank and paper coated with PVAc and its copolymers with lignin. The FE-SEM image shows that uncoated paper has a porous and open network structure with a non-uniform surface due to fiber entanglement on the surface of the paper (Figure 2A). In contrast, as shown in Figure 2B–F, the fibers and pores holes were covered with the coating materials. Therefore, the paper surface became smoother, and less pore structure was observed with increasing the lignin content in the copolymer. Anyhow, there was some difference in the coated paper appearance attributed to the differences in the viscosity of the copolymers. Indeed, the good interpenetration and interaction between paper and copolymers, which is attributed

to their chemical structure (composed of hydroxyl and acetate groups), leads to improve the mechanical and physical properties of coated paper.

Figure 2. Electron micrographs of the surface of the blank paper (A) and paper coated with PVAc (B), and coated papers with copolymers containing different fractions of lignin (C–F).

To study the effect of copolymers on paper wettability, the contact angle test was performed and the obtained results are shown in Figure 3. It was observed that the contact angles were increased from 2.1° for the blank paper to nearly 90° after coating. The coating with a copolymer containing 10% lignin showed the highest water-resistance with a water contact angle of 90° . The result showed that the copolymer can enhance the water-resistance of the paper, which is due to fact that lignin itself has a hydrophobic nature, although it is composed of multi hydrophilic groups.

Figure 3. The water contact angle of the blank paper and coated papers with PVAc and its copolymers containing different lignin fractions.

The values of the measured tensile index tear index and bursting resistance of the blank paper and coated paper shown in Table 1 and Figure 4. As shown in Table 1, the

tensile index and burst resistance have been significantly increased with the increase of the lignin content in the coated material, which may be because lignin-based copolymers can fill in between the fibers and enhance the adhesion of the fiber, thus hindering their sliding and stretching. From Figure 4, one can observe that the tensile index of coated papers increased significantly when the lignin fraction increased from 0% to 10% and then decreased slightly with the increase of lignin fraction in the copolymer. Because lignin molecules have a rigid structure, the coated paper with a copolymer containing a small fraction of lignin exhibited a good enhancement in the tensile index. These results agree with those reported in the literature [31–33].

Table 1. The values of ration, tearing, tensile, and bursting tests of the blank paper and paper coated with PVAc and its copolymers containing different fractions of lignin.

Test	Blank	0%	5%	10%	15%	20%
Ration (g/m ²)	86.435	108.330	105.119	111.158	109.837	103.043
Tear (mN.m ² /g)	11.666	7.821	7.759	7.956	7.403	7.214
Tensile (N.m/g)	43.848	72.740	73.187	81.596	64.368	61.528
Bursting (kPa.m ² /g)	2.742	5.040	5.280	5.285	4.575	5.192

Figure 4. The physical properties of the blank paper and the papers coated with PVAc and its copolymers containing different fractions of lignin.

On the contrary, the tearing index test of the coated papers showed a notable decrease. This is due to lignin having a rigid structure which forms a rigid film-like structure on the paper surface and makes the coated paper more brittle and reduces its tearing index.

3.2. UV and FTIR Spectroscopy Analysis

UV spectroscopy also was applied to monitoring the effect of PVAc and its lignin copolymers on the light properties of coated papers. Compared to the UV spectrum of the blank pape, the spectra of the coated papers are exhibited strong absorption peaks at 235 and 275 nm (Figure 5a) which associated with the phenolic structure of lignin (i.e., lignin

has a UV band that appears at 200–230 nm and 260–280 nm) [34]. It is worth mentioning that the UV absorption of coated papers seemed to be associated with the fraction of lignin in the copolymers. Due to the strength of the UV absorption, the transmittance values of the UV light (<400 nm) were neglected for the coated papers (Figure 5a), which indicates that the copolymers have similar properties to those polymers which are classified as UV-blockers. This finding is consistent with the literature reported by Parit et al. [35].

Figure 5. Ultraviolet (UV) and FTIR of the blank paper and paper coated with PVAc and its lignin copolymers containing different fractions of lignin, (a): UV absorption (b): FTIR absorption.

FTIR spectra of the blank and coated papers with PVAc and the copolymer are shown in Figure 5b. As seen, the blank paper has obvious intensity peaks of O–H vibration at 3319 cm^{-1} due to cellulose contains a large amount of –OH groups. Subsequently, after coating with copolymers, this peak weakened but still existed, indicating the interaction between paper and copolymers was achieved. Besides, the spectra of coated papers exhibited three new peaks at 1219 , 1365 , and 1737 cm^{-1} which are associated with CH_2 stretching, stretching of C–OH, the vibration of carbonyl C=O, and stretching vibration of C–O–C, respectively [36]. These results are indicating the presence of vinyl acetate on coated paper, and consistent with the literature [36,37].

3.3. Air Permeability Analysis and Thermal Stability Analysis

As expected, the coating with copolymer decreased air permeability. Figure 6 shows that the air permeability of the blank paper is 104.75 mm/s . Subsequently, after coating with copolymers, the air permeability was decreased significantly to the lowest level (30.275 mm/s) with 0% content of lignin in the copolymer. This is because the lignin-based copolymer could fill the gap between fibers, binding the fibers, reducing the porosity, and increasing the tightness, thereby reducing the air permeability. It is worth mentioning that lignin content in the copolymers affects the air permeability and it could be used to control the air resistance of paper. These results are consistent with SEM results and agree with the data reported in the literature [38,39].

The thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTGA) of the blank paper and paper coated with PVAc and its lignin copolymers containing different lignin fractions were carried out to investigate the effects of coating on the thermal properties of coated papers. As shown in the TGA curves (Figure 7a), all samples show three stages of loss in weight. In the first stage, a common behavior observed for all samples is the dehydration process, in which 8–12 wt.% of water was removed in the temperature range between 35 and $130\text{ }^{\circ}\text{C}$. The loss of mass in this stage depends on the initial moisture content of the samples. It was observed that there was a slight decrease in the amount of loss in weight after coating the papers. Besides, the blank paper has shown an ability to absorb more water than coated paper, possibly due to it having a more porous structure, as was seen in the SEM photographs. The DTGA curves, Figure 7b showed that the main thermal decomposition (in the second stage) of the blank paper happened very

fast and in the range of temperature between 290–410 °C and with a maximum degradation rate of 391 °C [40]. While the DTGA of papers coated with copolymer depicted a wide range of thermal decomposition (240–420 °C) and their maximum degradation temperature slightly decreased. This is due to the thermal degradation of vinyl acetate in PVAc and co-polymers takes place early [5]. Also, the presence of lignin molecules in copolymers creates a new inter-chain interaction with neighbor PVAc molecules (cross-linking) which restricts the motion of the main-chain [5,6]. Notably, the decomposition in this stage is due to the thermal-cracking reaction of C–C and C–O–C bonds (chain scission). The last phase of thermal decomposition happened at a temperature range of 420 to 600 °C; unlike the blank paper, the coated papers showed a higher loss in weight. The decomposition is due to the carbonization and evaporation of some volatile compounds (CO and CO₂) [41]. At the end of thermal degradation, the ash (carbon) content of the coated papers was higher than that of the blank paper.

Figure 6. The air permeability of the blank paper and paper coated with PVAc and its copolymers containing different fractions of lignin.

Figure 7. The thermogravimetric analysis (TGA) scans (a), and the derivative thermogravimetric analysis (DTGA) curve (b) of the blank paper and papers coated with PVAc and its lignin copolymers containing different fractions of lignin.

Figure 8 shows the differential scanning calorimetry (DSC) curves of paper coated with PVAc and its copolymer containing different fractions of lignin; all samples of coated papers displayed a well-defined glass transition (T_g). The paper coated with PVAc showed a sharp T_g at 43 °C, while all the papers coated with copolymers showed an obvious increase in their T_g s which reached 56 °C when the fraction of lignin in the copolymer was 20%. Besides, the T_g s peaks became broader thanks to the introduction of the phase change component of lignin molecules. These changes referred to the segment motion of the copolymer chains restricted as a result of the interaction between the copolymer and the surface of the paper [42]. The increases of T_g s of paper coated with the copolymer are attributed to the changes in the structure and crystallization behavior of the PVAc with the introduction of lignin molecules in its copolymers, as similarly reported by Nana Zhang [4]. Notably, the increase of T_g values was directly proportional to the amount of lignin fractions in the copolymers; this is due to the lignin's molecules are acting as a crosslinker between the neighboring molecules of the copolymers that leads to hindering their motion under heating, which implies enhancing the thermal stability as was suggested by Yao et. al [43] and Wang et.al [44]. Moreover, the DSC results are in good agreement with those obtained by thermogravimetric analysis (TGA) and the previous literature [5,6]. Thus, the fractions of lignin on the copolymer arguably have a significant impact on the thermal properties of PVAc, which leads to increases in the range of enthalpy relaxation and T_g s.

Figure 8. Differential scanning calorimetry (DSC) of papers coated with PVAc and its lignin copolymers containing different fractions of lignin.

3.4. Surface Free Energy (SFE)

The SFE of papers and paper-coated with copolymers samples in polar dispersive components were done based on the measured surface contact angle θ of the layer, the known free energy of the surface and the liquid was used to calculate the γ_S^P and γ_S^D by formal Equation (1), and the obtained results are shown in Table 2.

$$\gamma_L (1 + \cos \theta) = 2(\sqrt{\gamma_S^D} \times \sqrt{\gamma_L^D} + \sqrt{\gamma_S^P} \times \sqrt{\gamma_L^P}) \quad (1)$$

Table 2. Surface free energy and values of dispersion force of the blank paper and coated paper with PVAc and its copolymers containing different fractions of lignin.

Coated Paper	Contact Angle		$\gamma_s^P/\text{mJ}\cdot\text{m}^{-2}$	$\gamma_s^D/\text{mJ}\cdot\text{m}^{-2}$	$\gamma_s/\text{mJ}\cdot\text{m}^{-2}$	γ_s^P/γ_s^D
	θ_1	θ_2				
0%	14.2	86.4	3.83	28.02	31.85	0.1365
5%	23.1	85	5.19	26.63	31.82	0.1948
10%	23.2	92.8	2.18	26.61	28.79	0.0818
15%	15.7	80.0	6.41	27.83	34.25	0.2305
20%	14.4	107.4	0.01	28.00	28.01	0.0005

Note: θ_1 , θ_2 are the contact angles of benzene and water of coated paper, respectively.

As can be seen from Table 2, the surface free energy of the coatings with a lignin content of 10% and 20% was reduced by 9.6% and 12.1%. Compared to the paper coated with 0% of lignin, the γ_s^P/γ_s^D significantly reduced [45,46]. This indicates that the addition of a fraction of lignin reduces the surface free energy, and inhibits the diffusion of droplets on the surface which leads to improving the liquid-repellent performance of coated paper [47]. The dispersion force of the coating does not change much, because the dispersion forces on the solid surface are formed by the van der Waals force between the molecules [48]. The polar force of the surface free energy of the paper coated with copolymer decreased by 99.7%, because of the hydrophobic nature of lignin, which acted to form a hydrophobic layer on the surface after coating that reduced the surface free energy of the coated paper [49]. As a result, the water-resistance of the coated paper was enhanced significantly.

4. Conclusions

In summary, lignin-vinyl acetate copolymers with varying amounts of lignin of 0%, 5%, 10%, 15%, and 20% were successfully used for coating paper. The effect of lignin content of the copolymer on physical and mechanical properties was evaluated with different techniques. SEM micrographs showed that paper surface porosity decreased significantly when the paper was coated with copolymers; this is due to good interaction between copolymers and paper surface and to forming a continuous and smooth coating layer. Coating with copolymers enhanced the surface smoothness and increased the waterproof, air resistance, bursting, stiffness, and tensile strength of coated papers. Interestingly, paper coated with copolymers was shown to respond to UV absorption. Accordingly, it can be concluded that the application of lignin-vinyl acetate copolymer as a coating material for the paper provides a more homogeneous, smooth, and stable layer on its surface, which leads to adding multiple desirable properties to the paper and makes it more efficient in use.

Author Contributions: Conceptualization, S.W. and F.K.; methodology, N.Z.; validation, Y.Y.; investigation, P.L. and M.E.G.; writing—original draft, N.Z.; writing—review and editing, M.E.G.; supervision, S.W.; project administration, F.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key R&D Program of China (No. 2017YFB0308000) and the National Natural Science Foundation of China (Grant No.31971605. 31570566. 31600472).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available on request.

Conflicts of Interest: The authors declare no conflict of interest.

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