

PREPARATION AND PROPERTY ASSESSMENT OF ECO-FRIENDLY COMPOSITE BASED ON POLYVINYL ALCOHOL AND LIGNIN EXTRACTED FROM BIOMASS

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| ARTICLE INFO | ABSTRACT |
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| <p>Received: 12/11/2020</p> <p>Revised: 13/01/2021</p> <p>Published: 04/02/2021</p> | <p>Biodegradable composite films, based on polyvinyl alcohol (PVA) and lignin extracted from sugar bagasse, were fabricated with various weight ratios between two components. The composites show adequate characteristics contributed by PVA and lignin which have specific functional groups revealed by Infrared spectroscopy (FTIR). In addition, the composites possess outstanding characteristics including comparable optical and mechanical properties investigated by mechanical testing method and Ultraviolet-visible (UV) spectroscopy. The results also reveal that the mechanical properties of the PVA film containing 25% lignin are superior to the pristine PVA film and the composite supplemented by lignin has the ability of high absorbency of UV radiation, enabling the PVA/lignin composite film to be used as an eco-friendly material with UV-shielding property.</p> |
| <p>KEYWORDS</p> <p>Biodegradable composite</p> <p>PVA</p> <p>Lignin</p> <p>UV-vis</p> <p>Mechanical property</p> | |

NGHIÊN CỨU CHẾ TẠO VÀ ĐÁNH GIÁ TÍNH CHẤT MÀNG COMPOSITE THÂN THIỆN MÔI TRƯỜNG TRÊN CƠ SỞ POLYVINYL ALCOHOL VÀ LIGNIN CHIẾT TÁCH TỪ BÃ MÍA

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| THÔNG TIN BÀI BÁO | TÓM TẮT |
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| <p>Ngày nhận bài: 12/11/2020</p> <p>Ngày hoàn thiện: 13/01/2021</p> <p>Ngày đăng: 04/02/2021</p> | <p>Màng composite phân hủy sinh học trên cơ sở polyvinyl alcohol (PVA) và lignin chiết xuất từ bã mía đã được chế tạo thành công với các tỷ lệ khối lượng khác nhau giữa hai thành phần. Sản phẩm màng composite có đầy đủ các tính chất đặc trưng được tạo thành bởi hai vật liệu thành phần PVA và lignin. Cấu trúc hóa học và các nhóm chức đặc trưng của PVA và lignin được khảo sát thông qua quang phổ hồng ngoại (FTIR). Ngoài ra, tính chất cơ học và quang học của màng composite được đánh giá bằng phương pháp thử cơ tính và phương pháp hấp thụ phân tử UV-vis. Kết quả cho thấy, màng chứa lignin với hàm lượng 25% có cơ tính vượt trội hơn hẳn so với màng PVA ban đầu và lignin đồng thời tăng khả năng hấp thụ bức xạ UV của màng. Các tính chất này giúp màng composite PVA/lignin có thể ứng dụng làm vật liệu thân thiện môi trường có khả năng kháng tia UV.</p> |
| <p>TỪ KHÓA</p> <p>Màng phân hủy sinh học</p> <p>PVA</p> <p>Lignin</p> <p>UV-vis</p> <p>Tính chất cơ lý</p> | |

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1. Introduction

In recent years, environmental pollution has become a serious issue of global concern, which causes enormous adverse impacts on ecological balance, including climate change, land degradation, and desertification. As a result, sustainable development of each country has been threatened critically. Consequently, this alarming situation has drawn tremendous attention from society for wide range solutions. A large number of studies related to biodegradable materials which aims at replacing non-degradable plastic by eco-friendly materials have been conducted by numerous researchers.

In this context, bio-polymers such as lignin are used as components of biodegradable composites materials due to the diversity of properties and biodegradability. Lignin is a natural polymer playing a key role in the formation of plant cell walls. The chemical structure of lignin is formed by three main components: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S). The amount of every structural unit varies with plant species [1]. With complicated and diverse chemical structure, various lignin structure models have been proposed [2]. Lignin possesses several advantages such as low cost, low density, and comparable mechanical properties. In addition, lignin is extracted from biomass; therefore, products based on lignin pose no health risk. Due to their biodegradable, renewable, and mechanical properties, composites from lignin are considered prospective candidates to replace glass or carbon fiber-based synthetic composites. Lignin has the potential to be used as composites in construction, sport, packaging, and automotive industries [3], [4].

Lignin has been used with numerous petroleum-based resins to generate composites such as epoxy, unsaturated polyester, and some types of polyolefin. Among synthetic polymers, PVA has superior characteristics including nontoxicity, water-solubility, and hydrophilic with the presence of hydroxyl groups making it compatible with various biopolymer via the formation of hydrogen bonding at the interface [3]. Moreover, PVA possesses other properties such as biodegradability and high mechanical strength [4], [5]. Due to the diversity of its characteristics, PVA is used for many applications as water soluble films in agriculture and additives in textile, paper industries, and a variety of coatings. PVA is also utilized in composites with other polymers, especially natural polymers [6]. Therefore, there is a great amount of research associated with composites based on lignin and poly(vinyl alcohol) (PVA) [7], [8]. Some studies indicate that the linkage between polar polymers such as PVA and lignin is hydrogen bonding, which creates high degree inter-molecular interaction [8]. Besides, both PVA and lignin, and thus their composites are biodegradable, making them eco-friendly materials [9], [10].

Due to the outstanding properties of PVA and lignin, the experiments were conducted to fabricate composite films based on PVA and lignin extracted from bagasse according to previously published work [11]. In this study, the properties of composite films will be investigated, including surface morphology, mechanical properties, optical properties, and ultraviolet-shielding through some analytical methods.

2. Materials and methods

2.1. Materials

The bagasse for lignin extraction was collected as a by-product of the sugar companies in Tay Ninh province of Vietnam. Polyvinyl alcohol (MW: 205 000 g.mol⁻¹, 98-99% hydrolyzed) was supplied by Sigma Aldrich (Germany). Other chemicals with 99% purity were distributed by Guangdong Guanghua Sci-Tech Company (China).

2.2. Extracting lignin from sugarcane bagasse by using deep eutectic solvents (DESs)

The extracting process of lignin from sugarcane bagasse was referenced from a previous article [11]. The dry bagasse powder at about 224 μm was purified by Soxhlet equipment with

water and ethanol-benzene in turn. Then, this treated bagasse powder was put into DESs including choline chloride and formic acid (1:5 molar ratio) at 70°C for 3 hours with magnetic stirring at 200 rpm. The liquid containing DES-soluble lignin (DESL) was then obtained from the DESs-bagasse mixture by vacuum-filtering to remove hemicellulose and cellulose. After that, the DESL was diluted with ethanol, then centrifuged to isolate lignin. The obtained lignin was washed and dried to prepare for the next experiment.

2.3. Preparation of PVA/lignin composite films

PVA/lignin composite films were fabricated by the casting method. Firstly, PVA (M_w 205,000 $\text{g}\cdot\text{mol}^{-1}$) and lignin were put into distilled water successively. Then, the mixture was magnetically stirred and heated to 90°C. After that, this mixture was maintained at 90°C with a stirring time of 180 minutes to make PVA dissolve into hot water completely and lignin disperse homogeneously in the PVA matrix. After being cooled down to 70°C, the mixture was poured onto Petri dishes. Next, the mixture was dried in a vacuum oven at about 60°C to remove air bubbles. Then, the mixture is maintained at room temperature for 24h. Finally, the composites were removed from the Petri dishes and stored in a desiccator. For this experiment, the additional amount of lignin in the composite was investigated with 5 wt%, 15 wt%, 25 wt%, 35 wt%, and 45 wt%; thus, the samples were labeled as PL1, PL2, PL3, PL4, PL5 respectively and PL0 was referred to the pristine PVA sample.

2.4. Characterization

The appearance of specific functional groups in the chemical structures of PVA and lignin in composite samples was examined by Infrared spectroscopy (FTIR). The mechanical properties of the composite films, including tensile strength and elongation at break were investigated according to ASTM D882 standard using a tensile testing machine (Tensilon RTC-1210A, A&D Co., Ltd., Japan) with a tensile speed of 5 mm/min. The surface features of the samples were characterized by a scanning electron microscope (SEM, S4800-NHE, Hitachi, Japan). The ultraviolet radiation absorbency of the films was evaluated by a double-beam UV-Vis spectrophotometer (U-2910, Hitachi, Japan). To prepare for testing, all samples were fabricated with the same thickness at about 250 μm .

3. Results and discussion

3.1. Characterization of hydrogen bonding interactions between PVA and lignin in the composites

Chemical structures of PVA and lignin were illustrated by FTIR spectra (Figure 1). Lignin had adequate functional groups, revealed by specific peaks in FTIR spectra (Figure 1a). The peak at 1607 cm^{-1} indicated the presence of hydroxycinnamic ester in the lignin sample, 1360 cm^{-1} was associated with the structure of the syringyl lignin molecule breathing with C-O stretching, 1261 cm^{-1} corresponded to guaiacyl ring breathing with C=O stretching, 1208 cm^{-1} reflected the vibration of the C-O-C linkages in ethers and esters or phenolic hydroxyl, the band at 1125 cm^{-1} was associated with the C-H in-plane deformations vibration in syringyl aromatic ring types, and 1033 cm^{-1} originated from aromatic C-H in-plane deformation and C-O bending vibration in primary alcohols, guaiacyl type [11]. The specific peaks of PVA were shown at 3282, 2919, 1713, 1423, 1374, 1085, and 829 cm^{-1} , which were assigned to the O-H stretching vibration of the hydroxy group, CH_2 asymmetric stretching vibration, C=O carbonyl stretch, C-H bending vibration of CH_2 , C-H deformation vibration, C-O stretching of acetyl groups and C-C stretching vibration, respectively (Figure 1c) [7].

The hydrogen bonding interactions between PVA and lignin in the composites were demonstrated by FTIR spectra. Pristine PVA indicated hydroxyl (O-H) stretching vibration peak

at 3282 cm^{-1} and C-OH groups at 1085 cm^{-1} , (Figure 1c). In the composite sample (PL3) (Figure 1b), due to interaction with lignin, a redshift appeared from 3282 cm^{-1} to 3290 cm^{-1} for hydroxyl of PVA and a similar phenomenon occurred for C-OH groups which shifted from 1085 cm^{-1} to 1097 cm^{-1} . This redshift revealed the appearance of hydrogen bonding interactions between hydroxyl groups in PVA and polar groups in lignin, enhancing composite properties.

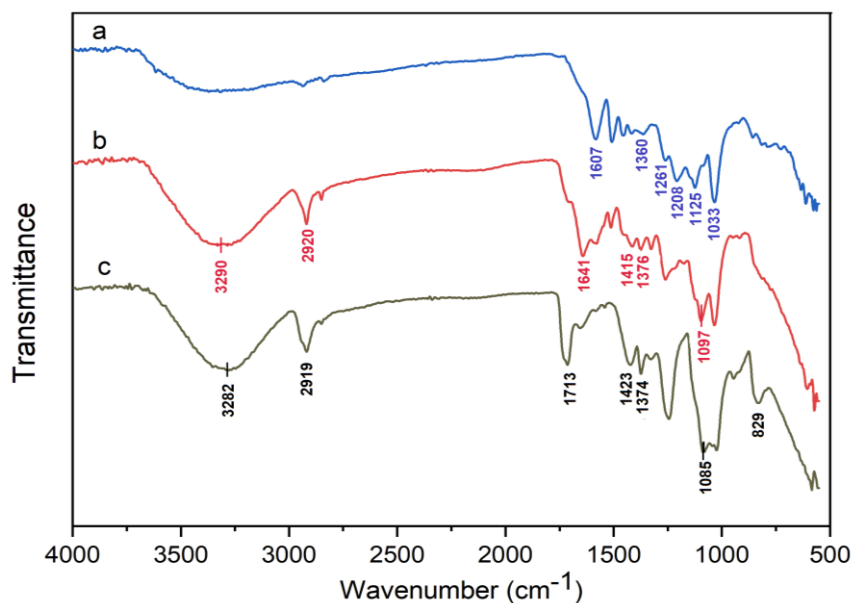


Figure 1. FTIR of lignin (a), PVA/lignin composite (PL3) (b), and PVA (c)

3.2. Surface morphology of PVA/lignin composite films

The surface morphology of composite film with 25 wt% lignin was observed by scanning electron microscopy (Figure 2).

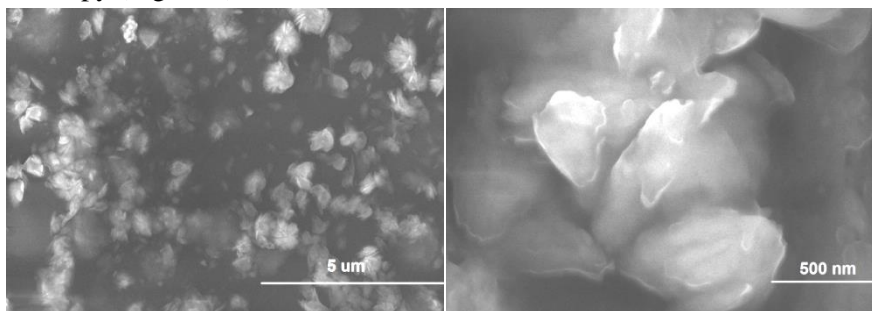


Figure 2. SEM image of composite film (PL3)

In the SEM image (Figure 2), it could be seen that the lignin was the discontinuous phase with particles size less than 500 nm and the PVA was the continuous phase. In addition, the result also showed that the sample surface had a uniform distribution and dispersion of lignin.

3.3. Mechanical property of the composite film

The effect of lignin content on the mechanical properties of PVA/lignin composite was illustrated in Figure 3. With the addition of lignin amount, the tensile strength of the composite increased gradually until the lignin content gained 25 wt%. Then, the tensile strength began to decrease when the lignin amount continued to be added. Therefore, the tensile strength of the sample reached the highest value of 62 MPa with the lignin content of 25 wt%, an increase of

about 35 MPa compared to the tensile strength of PVA film. It could be seen that lignin played a role as a filler in the composite, leading to an increase in the tensile strength of the film significantly. One of the reasons was that lignin obstructed the movement of PVA molecules under the impact of external forces, increasing the durability of the composite film. Another significant reason was because the bond between hydroxyl functional groups on lignin and PVA molecules created intermolecular hydrogen bonds in the composite structure, enhancing the tensile strength of the film. However, with more lignin content was added to the composite, only a part of the lignin tightly bound with PVA, the rest of the lignin poorly dispersed into the PVA matrix, leading to a decrease in the strength of the film.

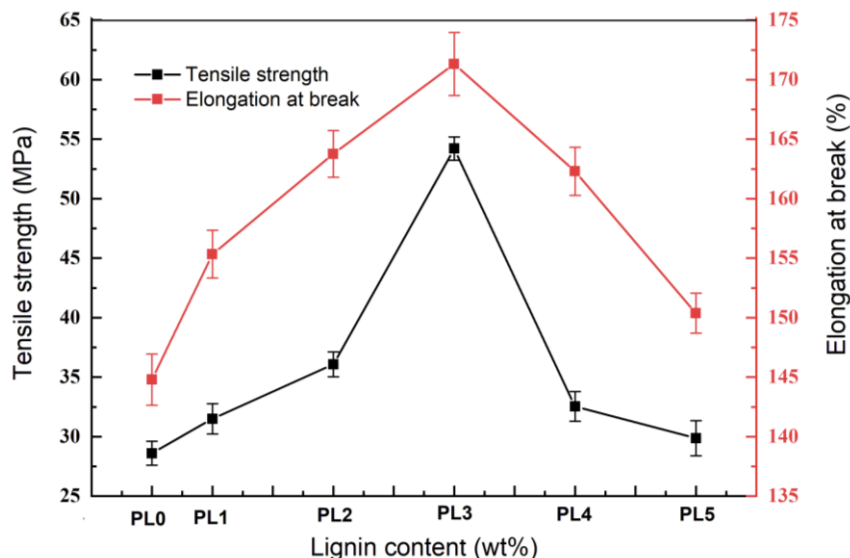


Figure 3. Mechanical properties PVA/lignin composites

Moreover, the elongation at break of the composite reached the maximum value of 171.3%, an increase of 32.5% compared with the PVA film. It could be seen that the lignin molecules are compactly linked with PVA molecules by hydrogen bonds. Therefore, under tensile force, lignin molecules stretched together with the PVA molecule, increasing the elongation of the composite. However, with higher lignin content, a part of lignin molecules clumped and acted as a poorly dispersed filler, reducing the ductility of the film, leading to a decrease in the elongation at break of the composite.

The maximum tensile strength and elongation at break of the composite were 62 MPa and 171.3% respectively with the lignin content at 25 wt%. As a result, PVA/lignin composite with 25 wt% lignin content had good mechanical properties and lignin acted as the filler strengthening the mechanical property for the film.

3.4. The UV-shielding performance of the composite film

According to the previous article, lignin is capable of absorbing UV radiation [11]. Therefore, lignin was added to PVA in order to improve the ultraviolet-shielding property of the PVA composite films, enabling this composite to be applied for a wide range of applications [12]. The UV-vis absorbency of PVA and the composite was revealed through the UV-vis spectra (Figure 4). The wavelength range was from 300 to 1100 nm.

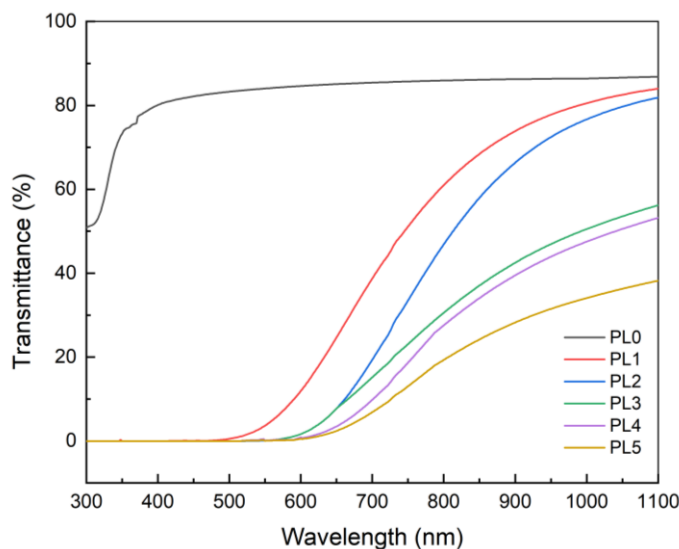


Figure 4. UV spectra of the samples

In particular, the UV spectrum less than 380 nm, and the visible light region from 380 to 500 nm were completely absorbed by the composite samples containing 5 wt% lignin. Whereas, the PVA sample without the addition of lignin allowed the majority of ultraviolet light to transmit, revealing that the PVA membrane had no UV-shielding property.

As shown in Figure 4, when the lignin content increased, the light transmittance of the PVA/lignin composite decreases significantly. The transmittance of light from 500 to 600 nm decreased to zero at the sample containing 15 wt% lignin, compared to 5 wt% lignin sample which transmitted about less than 20%. At 700 nm visible light, the transmittance of the samples with more than 15 wt% lignin reached from 15% to 20%, which was referred to shielding ability of 80%, an improvement of 63% compared to PVA film (17%).

In the infrared region (more than 1000 nm), the composites with 5 wt% and 15wt% lignin had a negligible decrease in transmittance compared to the PVA film. However, the light absorbency of the 45 wt% lignin sample was significantly improved. At 1100 nm, the transmittance of this film (PL5) was only about 35%, compared to 85% transmittance of PVA film (PL0).

It could be seen that the addition of lignin into the PVA matrix had significantly improved the light absorbency of the composite film, especially UV radiation. The more the lignin content added, the better the light absorbency reached. The composite with 45 wt% lignin gained the best light absorbency amongst the samples. Besides, all the samples containing lignin with the content from 15 wt% to 45 wt% could absorb a broad spectrum of UV light in the range of 300–400 nm. Therefore, the PVA/lignin composite containing 25 wt% lignin had both prominent properties including high mechanical property and good UV-shielding performance.

4. Conclusion

Composite films based on PVA and lignin have been successfully fabricated with different lignin contents, including 5 wt%, 15 wt%, 25 wt%, 35 wt%, and 45 wt%. SEM images show that lignin particles are evenly distributed in the film structure. Due to the good interaction between the two phases, lignin and PVA in the composite, the mechanical properties of the films are enhanced by adding the lignin if lignin content is not over 25%. The composite with a 25 wt% lignin has the best mechanical properties with a tensile strength value of 62 MPa, much higher than that of a pristine PVA sample. In addition, the UV resistance of composite films is also strengthened with the presence of lignin in the film. These results reveal that lignin is a potential biomass material, attracting a wide of many applications. Especially, PVA/lignin composite is

one of the outstanding applications due to its environmentally friendly features and high UV resistance.

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