INFLUENCE OF GLYOXAL CROSSLINKER ON SWELLING BEHAVIOR OF COMPOSITE HYDROGEL BASED ON LIGNIN AND POLY VINYL ALCOHOL

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ABSTRACT:

The composite hydrogel based on lignin and poly vinyl alcohol (PVA) was prepared by using glyoxal as crosslinker. The swelling property of the composite was investigated with varying the glyoxal concentrations. As the glyoxal contents increased from 10 wt% to 40 wt%, the swelling ratio of PVA-lignin composite decreased from 330 % to 95 %. Whereas, the gel fraction of the composite increased with higher glyoxal content. In addition, the surface morphology was observed by scanning electron microscopy (SEM) and the results showed that lignin was evenly distributed in PVA matrix. Moreover, specific functional groups of lignin and PVA molecules were revealed by Infrared spectroscopy (FTIR).

Keywords: composite hydrogel, lignin, PVA, glyoxal, swelling behavior.

1. Introduction

Recently, most of scientists pay much attention on researching hydrogel polymers due to their outstanding applications. Polymer hydrogels are hydrophilic network structure polymeric materials with the ability to absorb large amounts of water. Therefore, they are applied in numerous biomedical fields such as contact lenses, wound dressings, scaffolds, and drug-release materials. For instance, with application of drug-releasing, polymer hydrogels can insert drug inside them by the pores in hydrogel structure and then deliver drug into living body [1-3]. Moreover, due to their swelling property, polymer hydrogels are applied for water treatment by removing toxic heavy metal ions from wastewater. For example, PVA/chitosan blended hydrogel can absorb the cooper ion in the aqueous waste solution. [4].

Nowadays, various natural polymers are used in synthesizing hydrogel polymers. Among them, lignin is a remarkable candidate because of its specific properties. Lignin is a biopolymer which are extracted from biomass because it is a major constituent of natural biofibers in plants. Therefore, lignin is known as biodegradable

material and possesses the absorbing property due to the functional groups in lignin structure [5].

Poly vinyl alcohol (PVA) is a water-soluble polymer with functional chemical groups which can interact with other polymers to form hydrogel. PVA hydrogel possesses numerous advantages such as biodegradation, biocompatible, and high degree of swelling in water. Consequently, polymer hydrogels based on PVA and lignin are candidates for a range of application in biomedical and environmental fields [6,7].

In this study, lignin was extracted from sugarcane bagasse by following former researches [8]. In addition, PVA-lignin composite hydrogels were prepared with 25 wt% lignin content. And glyoxal was utilized as cross-linker for the hydorgel. Hydroxyl groups from PVA react with aldehydes of glyoxal via formation of acetal bonds [7]. The absorbency was investigated by the swelling ability. The Fourier transform infrared spectroscopy was also used to examinate specific functional groups of PVA and lignin in the hydrogel.

2. Materials and methods

2.1. Materials

PVA (average M_w = 205 000 g.mol^{-1}, 98-99% hydrolyzed) was purchased from Sigma Aldrich (Germany). Lignin (average M_w = 28265 g/mol as determined by GPC) was extracted from sugarcane bagasse [8], and glyoxal was obtained from Wako Chemical Industries, Japan. Other chemicals with 99% purity were distributed by Guangdong Guanghua Sci-Tech Company (China).

2.2. Preparation of PVA-lignin composite film

PVA and lignin were poured sequentially into reaction flask containing distilled water. The experiment was conducted at 90^{0}C with a stirring time of 180 minutes to get homogenous mixture. After that, the temperature of the reaction was decreased to 60^{0}C and glyoxal was put into the mixture. The mixture was continually stirred to get homogenous dispersion at constant temperature 60^{0}C.

Then proper weight of the mixture was put in glass Petri dish, followed by being cured at 80^{0}C for 90 minutes in an oven. After that, the sample was dried at 60^{0}C and was stored in a desiccator.

The weight percentage of lignin in the composite hydrogel was 25 wt%. The weight percentage of glyoxal, was investigated with 10 wt%, 20 wt%, 30 wt% and 40 wt% and the samples were named as PLG1, PLG2, PLG3, and PLG4 respectively.

2.3. Measurements

The dried composite samples were weighed (Wo), then were soaked in distilled water for 24 h to equilibrium swelling weight (Ws) for detaching soluble parts from film. After that, the film was dried at 60^{0}C in an oven and weighed again (We). The formulation for calculating the gel fraction was shown below [4]:

$$\text{Gel fraction (GF \%)} = \left(\frac{W_e}{W_o}\right) \times 100$$

For swelling test, the samples were cut into 1 x 2 cm piece, dried at 60^{0}C in an oven, and weighed (We). Then the dried samples were soaked in distilled water at 35^{0}C, then weighed (Ws) at interval times. The formulations of calculating the water uptake (swelling ratio) was shown below [4]:

Water uptake (swelling ratio)

$$\text{(SR \%)} = \left[\frac{(W_s - W_e)}{W_e}\right] \times 100$$

Moreover, the functional groups of PVA and lignin molecules were investigated by FTIR (Brucker Tensor 27, Germany).

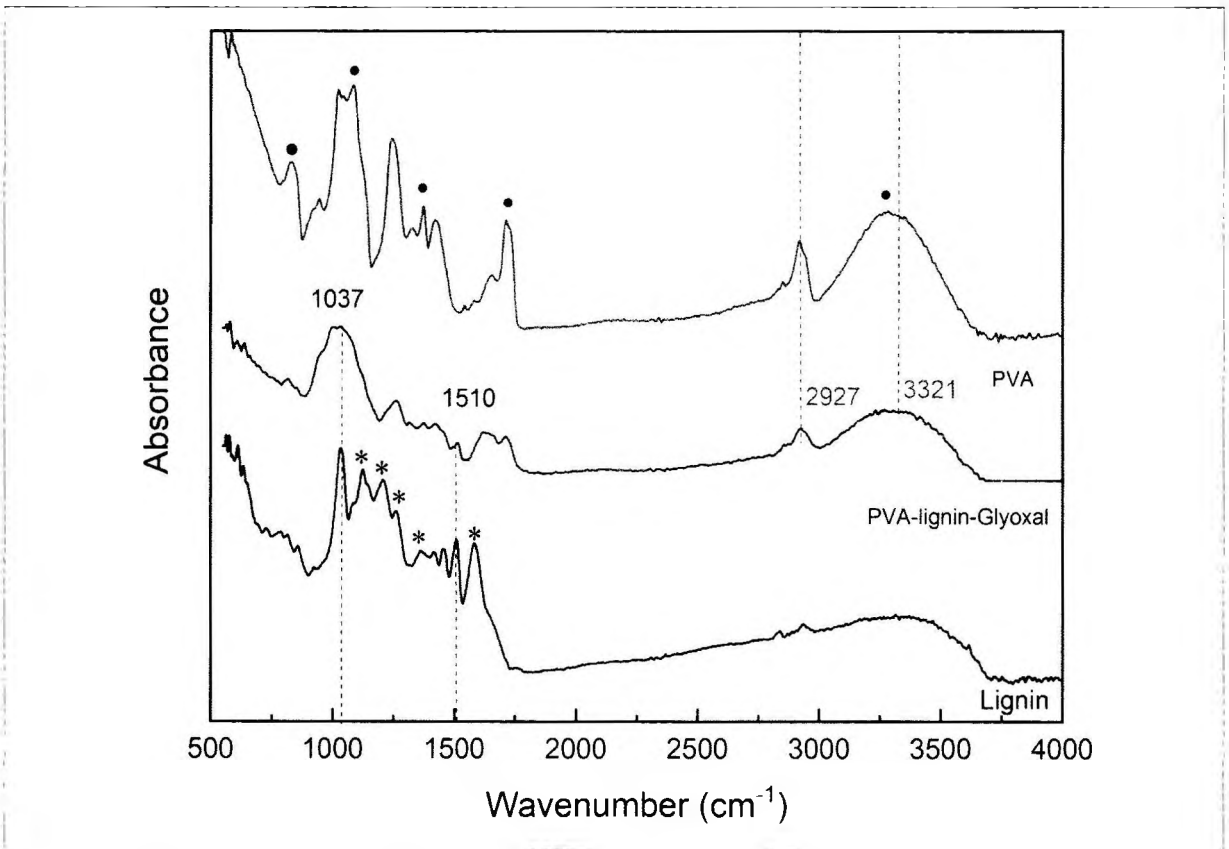
3. Results and discussion

3.1. Investigating characteristic functional groups of the composites by FTIR analysis

The cross-linked PVA-lignin film was characterized by FTIR spectra (Figure 1). The characteristic functional groups were shown with the samples including pure PVA, lignin, and PVA/lignin/glyoxal.

The lignin spectra showed that the peak appearing at 1598 cm^{-1} indicated the existence of hydroxylcinnamic ester in the lignin film. And

Figure 1. FTIR spectra of the lignin, PVA, and PVA-lignin composite

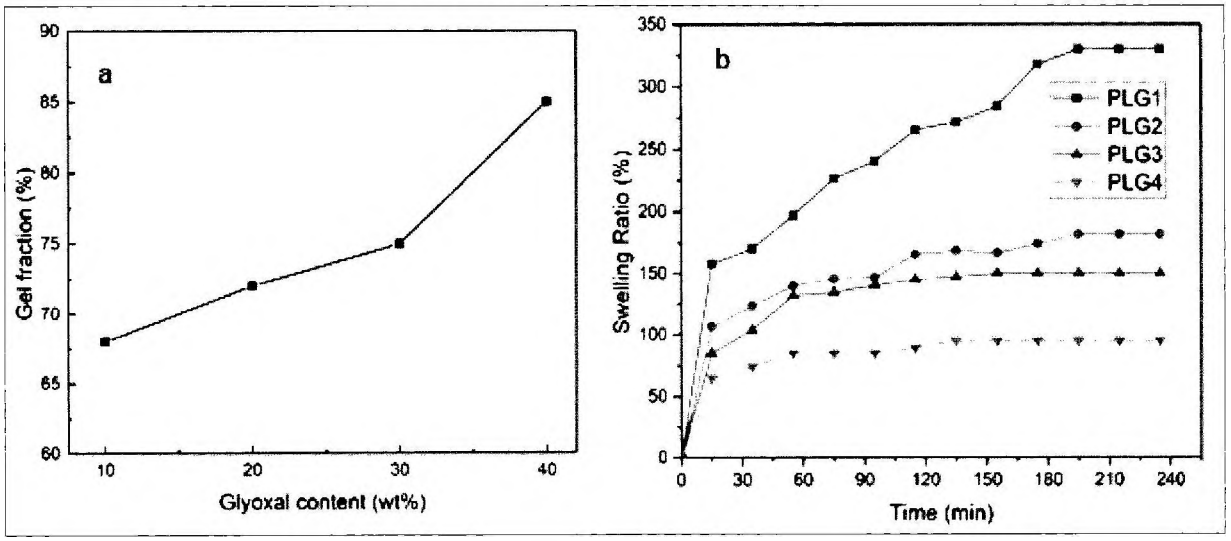


1510 cm^{-1} was attributed to the aromatic skeleton vibration in lignin. The peaks at 1389 cm^{-1} and 1267 cm^{-1} referred to the structure of the syringyl lignin molecule breathing with C-O stretching and guaiacyl ring breathing with C=O stretching, respectively. In addition, the peaks including 1205 cm^{-1} and 1127 cm^{-1} reflected the vibration of the C-O-C linkages in phenolic hydroxyl and the C-H in-plane deformations vibration in syringyl aromatic ring types, respectively. And the peak at 1037 cm^{-1} was associated -OH vibration in primary alcohols, guaiacyl type [8].

In the PVA spectra, the band from 3411- 3176 cm^{-1} reflected vibration of -OH group of PVA molecular. The peaks at 2927 cm^{-1} and 1380 cm^{-1} were associated with CH_2 asymmetric stretching vibration and CH deformation vibration. In addition, the peaks at 1715 cm-1, 1091 cm^{-1}, and 831 cm^{-1} were assigned to C=O carbonyl stretch, C-O stretching of acetyl groups and C-C stretching vibration, respectively [8].

The spectra of PVA-lignin-glyoxal illustrated the peaks at 1510 and 1037 cm^{-1} of lignin. And the peaks concerned to -CH2 (2927 cm^{-1}) and -OH vibrations of PVA spectra also appeared. Comparing to the spectrum of pristine PVA which showed -OH vibration peak at 3276 cm^{-1}, the spectrum of composite showed the redshift of hydroxyl (-OH) from 3276 cm^{-1} to 3321 cm^{-1}. The reason for this phenomenon could be hydrogen bonding formation between hydroxyl groups in PVA molecular and polar groups in lignin chain. Moreover, due to cross-linking formation between hydroxyl of PVA with glyoxal, the absorbance at the wavenumber reflecting hydroxyl group decreased compared to PVA. This could be the result of consuming hydroxyl groups for linkage with aldehyde group in glyoxal.

Figure 2. Gel fraction and swelling ratio of the composites



3.2. Effect of glyoxal contents on gel fraction and swelling behavior

Figure 2 illustrated swelling study of the composite film versus glyoxal contents. At the beginning of the experiment, the samples were soaked into distilled water at 35^{0}C. After 15 min, small amounts of PVA-lignin were dissolved into water. The dissolved amounts increased and reached maximum value, which equilibrium swelling weight, after 24h. This was caused by PVA-lignin portions which did not crosslink and transferred into water. Therefore, the dissolved portions depend on the glyoxal contents. The more glyoxal contents were used, the more crosslinked portions of the composites have been formed. Consequently, the composite with more content of glyoxal had more cross-linking density and therefore had higher gel fractions (Fig. 2a).

Moreover, the glyoxal contents also affected the swelling ratio (the water uptake) of the composite. Generally, at high glyoxal content, the composite the composite had the low swelling ratio about 95 % with the PLG4 sample. When the glyoxal content reduced from 40 wt% (PLG4) to 10 wt% (PLG1), the swelling ration progressively increased to 330% (Fig. 2b). This is due to, the high glyoxal content caused the high crosslinked structure in the composite. Therefore, the more -OH groups were consumed in the crosslinking reaction between PVA and glyoxal. Consequently, the composite

Figure 3. SEM image of PLG1 composite

reduced its hydrophilicity and could not absorb much water, contributing to the low swelling ratio.

3.3. Surface morphology of PVA/lignin composite films

It could be seen the surface morphology of the composite film through SEM image (Fig. 3). In the SEM image of PLG1 sample, the lignin dispersed in the PVA matrix homogenously. The lignin particle size about 500 nm was observed by the image.

4. Conclusions

In summary, the composites based on lignin and PVA crosslinked with glyoxal were prepared successfully. The swelling ratio and gel fraction were changed with varying glyoxal concentrations from 10 wt% to 40 wt%. Increasing glyoxal contents made the composites possess higher crosslinking degree in their structure, leading to high gel fraction and low swelling ratio. With 10 wt% glyoxal, the PLG1 sample obtained maximum swelling ratio with 330%. In addition, the composites had good surface morphology with homogenous dispersion of lignin in PVA matrix through SEM image. Moreover, the FTIR spectra revealed that the composites had adequate specific chemical groups of lignin and PVA molecules ■

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ẢNH HƯỞNG CỦA GLYOXAL ĐẾN ĐẶC TÍNH TRƯƠNG NỞ CỦA HYDROGEL COMPOSITE TRÊN CƠ SỞ LIGNIN VÀ POLY VINYL ALCOHOL

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TÓM TẮT:

Hydrogel composite trên cơ sở lignin và poly vinyl alcohol (PVA) đã được chế tạo thành công với chất đóng rắn glyoxal. Tính chất trương nở của composite đã được khảo sát với sự thay đổi các nồng độ glyoxal khác nhau. Khi hàm lượng glyoxal tăng từ 10% lên 40%, tỷ lệ trương nở của composite PVA-lignin giảm từ 330% xuống 95%. Trong khi đó, tỷ lệ gel của composite tăng lên khi tăng hàm lượng glyoxal trong hỗn hợp. Ngoài ra, phương pháp kính hiển vi điện tử quét (SEM) được sử dụng để quan sát hình thái bề mặt của composite và kết quả cho thấy lignin phân tán và phân bố đồng nhất trên nền PVA. Bên cạnh đó, các nhóm chức hóa học đặc trưng của các phân tử lignin và PVA trong hydrogel composited đã được khảo sát bằng phương pháp quang phổ hồng ngoại (FTIR).

Từ khóa: composite hydrogel, lignin, PVA, glyoxal, swelling behavior.