# Preparation and Characterization of Lignin-based Membrane Material

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Lignin-based membrane material was prepared from lignosulfonate extracted from sulfite pulping. The effects of formaldehyde, polyvinyl alcohol (PVA), urea, borax, glutaraldehyde (GD), and dimethyl phthalate (DMP) on tensile strength and water absorption were investigated. The experimental results showed that the optimum conditions were as follows: a reaction temperature of 85 °C, 22.22 wt.% lignosulfonate, 1.59 wt.% borax, 22.22 wt.% urea, 31.75 wt.% formaldehyde, 22.22 wt.% PVA, 32.32 wt.% GD (to PVA glue), and 32.32 wt.% DMP (to PVA glue). Under these conditions, the tensile strength reached $2.2 \times 10^4$ Pa and the water absorption was 35.2%. The products were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The results showed that the product components were compatible in this system, and the introduction of cross-linking agents may have resulted in a decrease in pore size.

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## INTRODUCTION

In nature, lignin is the second most abundant renewable resource, after cellulose. Because of the complicated structure of lignin, its applications are limited in industry and agriculture and its utilization rate is very low. The target product produced in pulping process used to be called "contaminant". Actually, the waste liquid from papermaking is mostly lignin degradation products, which can be regarded as a renewable carbon resource. Modified lignin can have a high molecular weight and enhanced surface activity (Mu *et al.* 2006). Consequently, modified lignin products have useful applications in many fields: concrete admixtures, oil exploration, dispersing of dyes, controlled-release fertilizer, and synthetic wood. These uses broaden the scope of application and improve the utility value of lignin. Industrial lignin is a valuable, available, non-toxic, biodegradable resource. By conducting in-depth research in this field, there is potential to achieve efficient use and recycling of resources (Cao 2003; Zhong 2003). As a result, new methods of developing and utilizing lignin are an emerging research topic (Li *et al.* 2014).

There are many domestic products that are generally good at fixing dry sand, such as emulsified asphalt, emulsified oil, modified polyvinyl alcohol, modified silicate (Hu *et al.* 1997; Gong *et al.* 2001). However, these products can have high costs, difficult biodegradation, and significant contributions to environmental pollution. LignoTech company reported that lignosulfonate can be used for sand-fixation, prevention of dust, and

roadbed reinforcement. However, the intensity of sand-fixation and rain erosion resistance is poor with unmodified lignosulfonate.

In this paper, lignosulfonate extracted from sulfite pulping was modified to increase water resistance (Pei *et al.* 2008), to provide good mechanical properties, and to achieve low water absorption. This technology was intended to be applied in the windbreak and sand fixation sectors, to reduce the impact of the particulates on the environment (Liao and Luo 2004). The goal of this study was to obtain a completely biodegradable composite material, which could play a significant role in industrial and agricultural applications (Tian 1999; Kapanen *et al.* 2008).

## EXPERIMENTAL

### Materials and Equipment

Sodium lignosulfonate was supplied by Quanlin Paper Industry Co., Ltd in Shandong Province, China. All other reagents were of analytical grade and were used as received. The mechanical properties of the materials were measured with a TTM-500A computer tensile testing machine (China, Changchun Yongxing Instrument Co., Ltd). Infrared (IR) spectra were recorded using a TENSOR27 FTIR spectrometer (Germany, Bruker Optics) in the range of 4000 to 400 $cm^{-1}$. Scanning electron microscopy (SEM) images were taken on a JSM-6700F scanning microscope (Japan, Japanese Electronics Co., Ltd). The sample was coated with a thin layer of gold in a vacuum before examination. Differential scanning calorimetry (DSC) was performed in the temperature range of 20 to 220 °C at a heating rate of 10 °C $min^{-1}$ in a nitrogen atmosphere (Germany, NETZSCH, STA 2500 Regulus).

### Preparation of Lignin-based Materials

The lignin-based materials were prepared by mixing two separate homogeneous solutions. First, a homogeneous solution of polyvinyl alcohol (PVA) was prepared by adding glutaraldehyde (GD) and dimethyl phthalate (DMP) to PVA and stirring at 90 °C for one hour. Second, the materials were prepared by uniform mixing of the prepared solution and the sodium lignosulfonate solution. After stirring at 85 °C, borax was added and allowed to react for 0.5 h. Then formaldehyde was added. In half an hour urea was added and stirred in well. The casting solution was cast on a glass plate using a doctor blade and the blade height was 0.12 mm. The material was dried and maintained at ambient conditions.

### Tensile Testing

According to GB/T 453-1989, tensile tests (Li *et al.* 1996) of the materials were performed on a TTM computer tensile testing machine equipped with a 500-N cell, and the rate used in the test was 25 mm/min. Five replicates were performed to obtain an average value.

### Water absorption

The water absorption was calculated using the following equation:

$$Q = \frac{W_w - W_d}{W_d} \times 100\% \tag{1}$$

where $W_w$ and $W_d$ are the weights of the wet and dry membranes, respectively.

## BIODEGRADABILITY TEST

Membranes were cut into six parts, each of them having dimensions of 100 mm × 100 mm. After being weighed, each was buried into the 5 cm pot at the same living criterion, the relative humidity was about 65%. After 7, 14, 21, 35, 49, and 56 days, each sample was taken out, cleaned, dried, and weighed. The biodegradation rate was calculated using the following equation:

$$W = \frac{m_0 - m_1}{m_0} \times 100\% \tag{2}$$

where $m_0$ and $m_1$ are the weights of before degradation and after degradation, respectively.

## RESULTS AND DISCUSSION

### Factors of the System
*Effect of PVA dosage*

Figure 1 shows that tensile strength increased with increasing PVA dosage to reach a maximum value, then decreased. The water absorption decreased with increasing PVA dosage to reach a minimum value, then increased. This phenomenon may occur because a large number of hydroxyl groups in PVA can crosslink with the free hydroxyl groups in the system, improving the mechanical properties and water resistance of the membranes. With increasing PVA dosage, the crosslinking equilibrium of the system was destroyed. The results showed that the system should be prepared with a PVA dosage of 22.22%.
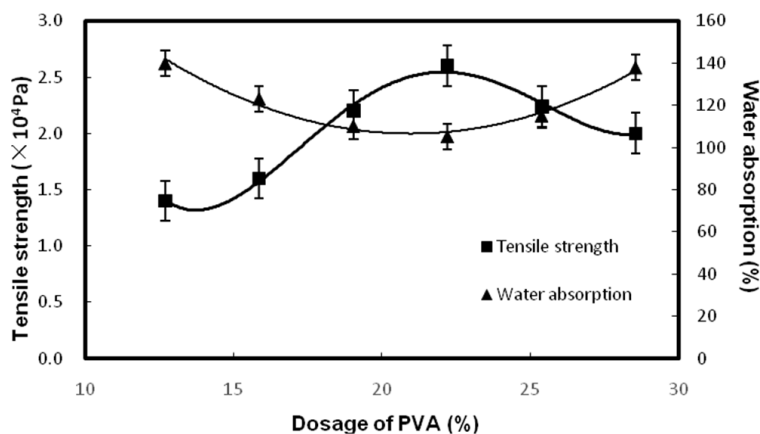


**Fig. 1.** Effect of PVA dosage on tensile strength and water absorption

*Effect of GD dosage*

Figure 2 shows that tensile strength increased with increasing GD dosage (w/w % PVA glue), then decreased, and water absorption reached 30.52% when the GD dosage was 32.32%. This phenomenon may occur because GD can crosslink with lignosulfonate in the system, improving the mechanical properties and water resistance of the membranes.

With increasing GD dosage, the crosslinking equilibrium of the system was destroyed. The results showed that the system should be prepared with a GD dosage of 32.32%.
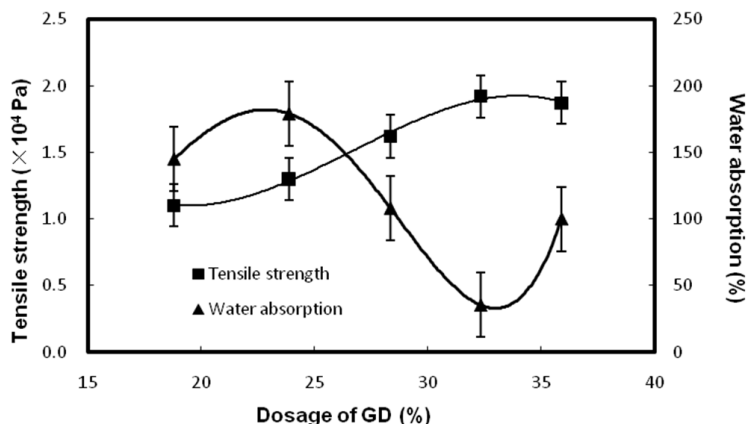


**Fig. 2.** Effect of GD dosage on tensile strength and water absorption

*Effect of DMP dosage*
Figure 3 shows that tensile strength increased with increasing DMP dosage (w/w% PVA glue) to reach a maximum value, then decreased; water absorption showed a contrary tendency. This phenomenon may be explained by the fact that DMP is a plasticizer (Chen *et al.* 2008), which improved the mechanical properties and water resistance of the membranes. The results showed that the system should be prepared with a DMP dosage of 32.32%.
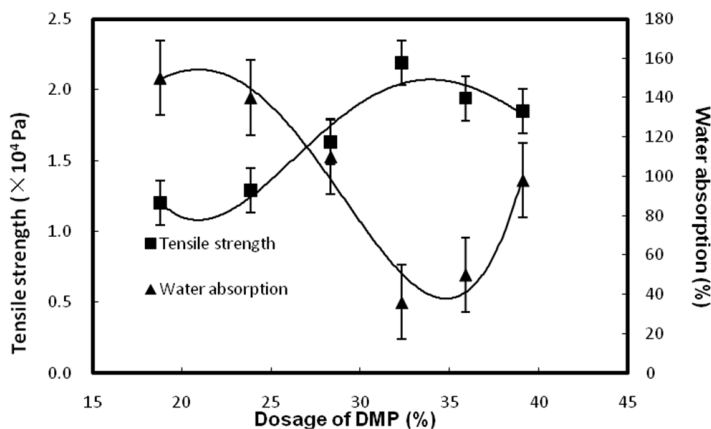


**Fig. 3.** Effect of DMP dosage on tensile strength and water absorption

*Effect of borax dosage*
The effect of borax dosage on the tensile strength and water absorption of the materials is shown in Fig. 4. Tensile strength increased, while the water absorption caused no apparent change with increasing borax dosage. This result may be ascribed to the ability of borax to react with the high amounts of free hydroxyl in the system. The borax was as thickening agent and preservative, so it has little effect on water absorption. When the mass ratio of borax to the system exceeded 1.7%, the viscosity of the system proved too great to form a membrane. Consequently, a borax dosage of 1.59% resulted in the best tensile strength and water absorption.
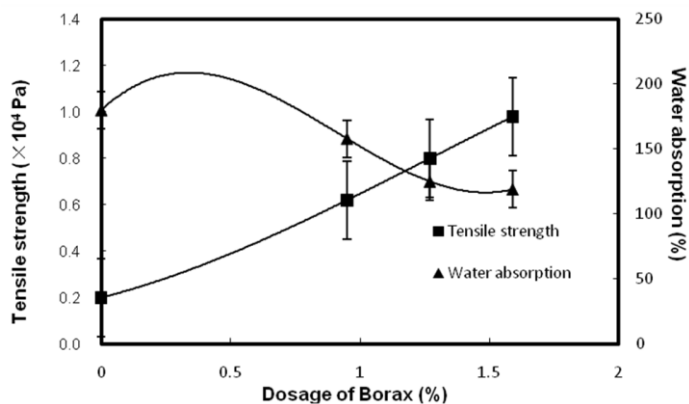
**Fig. 4.** Effect of borax dosage on tensile strength and water absorption

*Effect of formaldehyde dosage*

Figure 5 shows the effect of the mass ratio of formaldehyde in the system on tensile strength and water absorption as other reaction variables remained constant. Tensile strength initially increased, followed by a decrease with increasing formaldehyde dosage. Conversely, the water absorption decreased with increasing formaldehyde dosage, then increased.

This phenomenon may be explained by the occurrence of a condensation reaction between formaldehyde and sodium lignosulfonate (Ren and Fang 2005), which increased the viscosity and molecular weight of the condensation product. At the same time, reducing hydrophilic groups resulted in a decrease in water absorption. However, with the increase in formaldehyde dosage, a Cannizzero reaction between lignosulfonate and formaldehyde would happen (Wang *et al*. 2011), and the cross-linked balance between formaldehyde, PVA, and sodium lignosulfonate was destroyed.

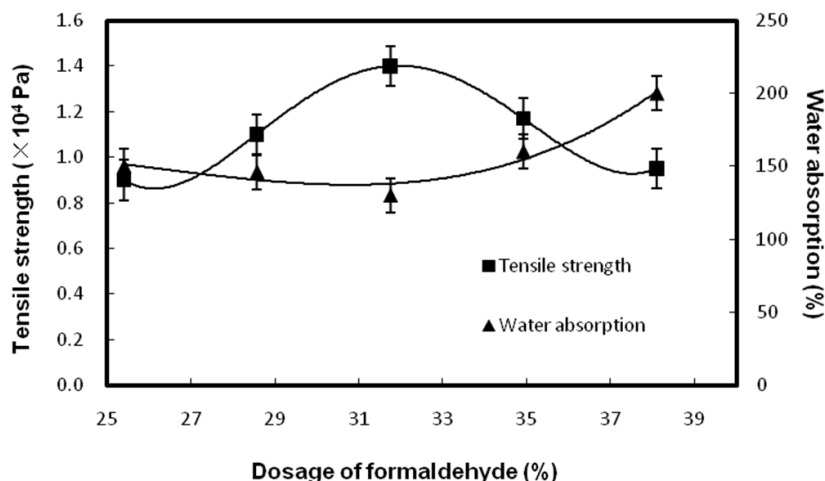The results showed that the system should be prepared with a formaldehyde dosage of 31.75%.



**Fig. 5.** Effect of formaldehyde dosage on tensile strength and water absorption

*Effect of urea dosage*

Figure 6 shows that, while tensile strength increased with increasing urea dosage to reach a maximum value before decreasing, water absorption showed a contrary tendency. This phenomenon may occur because the active hydrogen atom of the amine groups in urea

can react with the carbonyl group of formaldehyde, generating a hydroxyurea, which causes a further reaction of formaldehyde. Because of the dehydration cross-linking process that formed the structure of the "lignin-urea formaldehyde-lignin" in the system (Jin and Liu 2006), the mechanical properties and water resistance of the membranes improved. As urea dosage increased, the reaction equilibrium was destroyed.

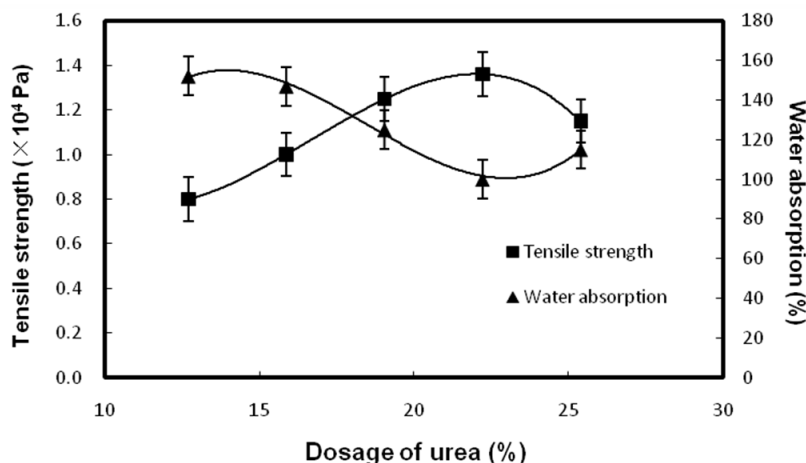The results showed that the system should be prepared with a urea dosage of 22.22%.



**Fig. 6.** Effect of urea dosage on tensile strength and water absorption

## Characterization of Lignin-based Material

*Fourier transform infrared spectroscopy (FTIR)*

Figure 7 shows the FTIR (Qiu 2008) spectra of sodium lignosulfonate, PVA, and the lignin/PVA composite membrane.
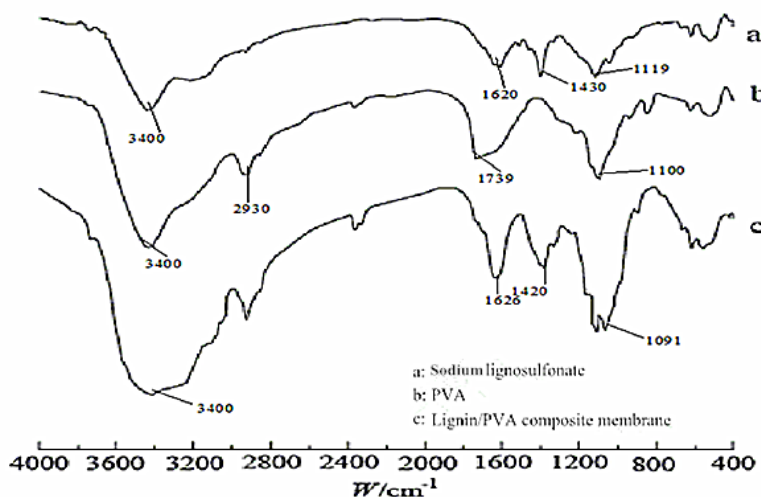


**Fig. 7.** FTIR spectra of (a) sodium lignosulfonate, (b) PVA, and (c) lignin/PVA composite membrane

As shown in Fig. 7, the spectrum of sodium lignosulfonate showed the O-H stretching vibration at 3400 cm$^{-1}$ and the characteristic absorption peak of C-O at 1119 cm$^{-1}$. The spectrum of PVA showed the C=O bond characteristic absorption peak at 1739 cm$^{-1}$. A different infrared spectrum was observed for the lignin/PVA composite membrane,

the peak at 1420 to 1091 cm$^{-1}$, which was the absorption peak shifted to lower wave numbers, indicating that the structure of the material had changed. The peak at 1626 cm$^{-1}$ confirmed that the PVA and sodium lignosulfonate were copolymerized.

*SEM observation*

Figure 8 shows that the pore size of the membrane prepared from a mixture of sodium lignosulfonate and PVA decreased and the density of the membrane increased when treated with crosslinking agent. This phenomenon may have arisen because the strong interaction (Luo 2001) between sodium lignosulfonate and PVA destroyed their cohesion, allowing both components to reach compatibility.
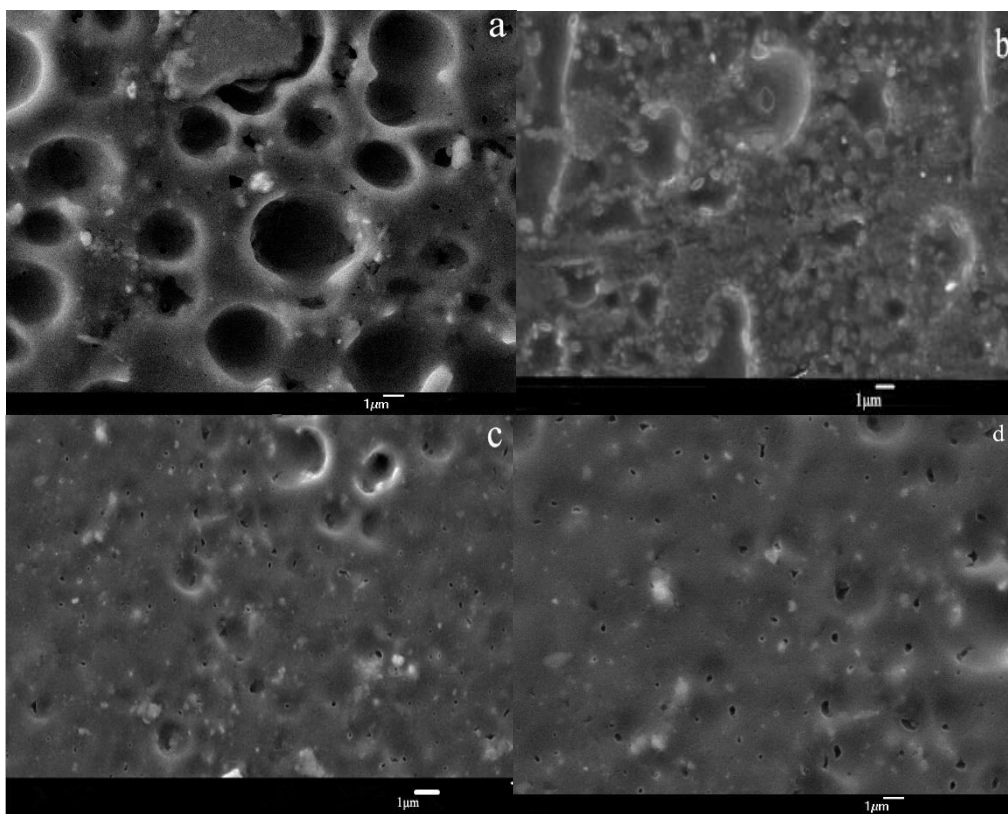


**Fig. 8.** SEM of the distribution of (a) mixture of sodium lignosulfonate and PVA, (b) add borax, (c) add formaldehyde, and (d) lignin/PVA composite membrane

*Differential scanning calorimetry (DSC)*

The compatibility of a blend membrane is important for its application, and one of the most commonly used methods to estimate the compatibility of a blend membrane is determining the glass transition temperature compared to that of the component polymers (Chen and Sun 2013).

DSC (Zhao *et al.* 2013) thermograms of sodium lignosulfonate, PVA and their blends are displayed in Fig. 9, which shows that the lignin/PVA blends exhibited values (105.1 °C, 180.1 °C) between the values (72.6 °C and 107.6 °C,165.1 °C, and 187.6 °C) of their parent polymers, sodium lignosulfonate and PVA, indicating the compatibility of their blends.
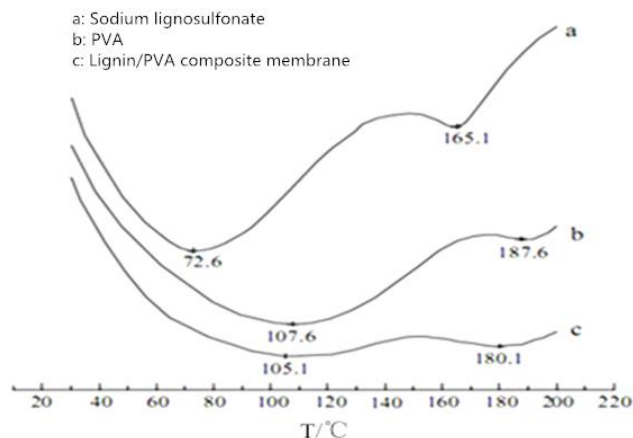
**Fig. 9.** DSC thermograms of (a) sodium lignosulfonate, (b) PVA, and (c) the composite membrane

*Biodegradability*

As shown in Fig. 10, the degradation rate of materials increased with soil burial time. Degradation rate rose from 13.3% on the 7$^{th}$ day to 75% on the 56$^{th}$ day. The experimental results showed that materials have good degradable properties.

Lignin-based membrane material mainly consisted of lignosulfonate and PVA. There are many active hydroxyl groups on PVA, which is a kind of degradable polymer material (Zhao *et al*. 2009). Some studies have shown that humidity and microbes are the main factors affecting degradation. Firstly, lignosulfonate and PVA contain a lot of hydroxyl groups. Hydrophilic groups of lignin-based materials contribute to water-soluble character, and they can change the structure and proportion of materials. Consequently, humidity has a great accelerating effect on the ageing rate. Secondly, under the conditions of microbes, the increase of soil carbon source and water can create favorable conditions for microorganism living activity. Microbes can reduce the crystallinity of membrane materials and produce dioxide and water (Tang *et al*. 2010). In conclusion, synergy of two facts speeds up the degradation rate of lignin-based materials.
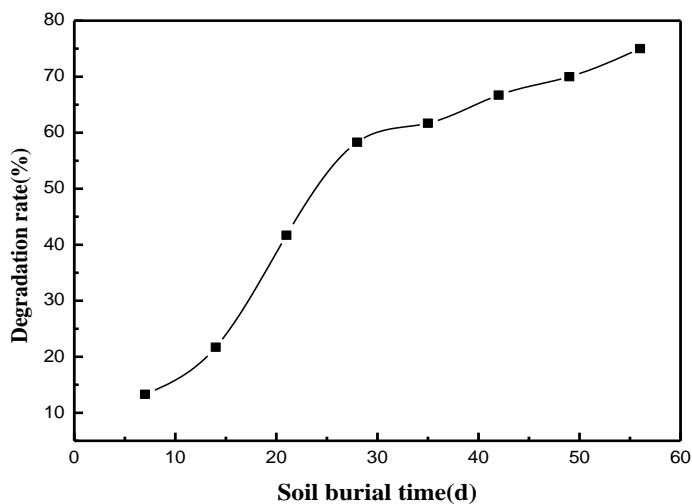


**Fig. 10.** Degradation rate curve of materials

*Comparative data of physical properties*

Contrast tests have been conducted between obtained material and PE mulch, which are shown in Table 1. During testing, dry tensile strength of obtained material was found to be 1.5 times higher than PE mulch, and the wet tensile strength was 0.61 times higher than PE mulch. Tearing strength and bursting strength of obtained material close to PE mulch, while the elongation of obtained material was much lower than PE mulch. Consequently, the results showed that obtained material meets product requirements.

**Table 1.** Comparison between PE Mulch and Lignin-based Material

|  | Tensile strength （×10⁴ Pa） | Elongation （%） | Tearing strength （N） | Bursting strength （kPa） |
|---|---|---|---|---|
| PE mulch | 0.87 | 124.33 | 2.08 | 96.7 |
| Lignin-based material | Dry2.2  Wet1.4 | Dry99.05  Wet102.30 | 2.60 | 97.5 |

## CONCLUSIONS

1. Lignin-based materials were fabricated. Efficient reaction conditions were confirmed by single-factor experiment.

2. The efficient reaction conditions were as follows: a reaction temperature of 85 °C; 22.22 wt.% lignosulfonate, 1.59 wt.% borax, 22.22 wt.% urea, 31.75 wt.% formaldehyde, 22.22 wt.% PVA, 32.32 wt.% GD (to PVA glue), and 32.32 wt.% DMP (to PVA glue).

3. Under the conditions of conclusion 2, the tensile strength of this lignin-based material reached $2.2 \times 10^4$ Pa and the water absorption was 35.2%.

## ACKNOWLEDGMENTS

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