

Preparation and Properties of Liquefied Banana Pseudo-stem based PVAc Membrane

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A series of novel membrane materials were prepared based on liquefied banana pseudo-stem (LBPS) blended with various proportions of polyvinyl acetate emulsion (PVAc). The mechanical properties, structure, thermal stability, and cross-sectional morphologies were investigated using a universal testing machine, Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM), respectively. The addition of LBPS to PVAc led to a structural change, and this change depended on the reaction temperature. The enhancement of elongation and the thermostability of membranes is attributed to an increase in C-O-C groups. Furthermore, the LBPS/PVAc membranes have a higher water resistance.

Keywords: Polymer membranes; Banana pseudo-stem; Liquefaction; Polyvinyl acetate

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INTRODUCTION

Agricultural by-products, *e.g.* corn straw, wheat straw, and banana pseudo-stem, which primarily consist of cellulose, hemicellulose, and lignin, represent a disposal problem because they can lead to biomass spoilage and environmental pollution. Banana is a kind of conventional fiber resource in south China, India, Ecuador, and the Philippines. After harvesting the fruit, copious amounts of banana pseudo-stem are produced. There is a great need to find value-added uses for banana pseudo-stem, which is a grossly under-utilized resource in many countries. The softness and relatively easy mechanical breakdown of the material suggests to people that it should be suitable for processing into various items. The authors have considered liquefaction as one such treatment in combination with polyvinyl acetate (PVAc).

Liquefaction is a convenient and effective technology for converting lignocellulosic biomass into fragments of small molecules that have good flow ability. At the same time, these fragments are unstable and reactive; they will be re-polymerized or re-condensed into liquid compounds with appropriate molecular weights (Demirbas 2001). Recently, liquefaction of lignocellulosic materials have been developed by using polyhydric alcohols in the presence of acid catalyst at an appropriate charge ratio of raw material to liquefying solvents under atmospheric pressure (Hassan and Shukry 2008) to produce low-molecular-weight bio-based polyols, which are rich in multifunctional hydroxyl groups.

Biomass-based polyols that are obtained by liquefaction play a key role in the synthesis of polymeric materials and polymer additives, such as in the preparation of polyurethane films (Kurimoto *et al.* 2001), polyurethane foams (Cinelli *et al.* 2013; Yan *et al.* 2008), epoxy resin (Zhang *et al.* 2012), and plasticizers (Azwar *et al.* 2013). It has been found that the plasticizers can be formed through an esterification reaction with acetic acid

and a catalyst (dibutyl-tin (IV) oxide) to form biopolyols. However, this kind of catalyst is usually toxic and expensive, rendering this esterification modification inappropriate in the developing processing industry.

Polyvinyl acetate (PVAc), a thermoplastic polymer, has advantages such as biodegradability and non-toxicity. Therefore, it is widely used in civil engineering, paper processing, packaging, and adhesives. However, the low heat resistance and the poor water resistance of PVAc have limited its application, particularly in hot and humid environments. Research has been done to modify such properties, often by means of copolymerization and blending (Kaboorani and Riedl, 2011a,b; Kaboorani *et al.* 2012; Peruzzo *et al.* 2014; Zhang *et al.* 2013). With respect to the blending method, the addition of polymers (*e.g.*, melamine formaldehyde resin) into the PVAc is of great interest in materials processing. The miscibility of polymers and PVAc is due to the strong inter-association hydrogen bonding between the hydroxyl group of polymer and the carbonyl group of PVAc (Kim and Kim 2005).

Meanwhile, adding polymers to PVAc may trigger some cross-linking reactions in the PVAc. The cross-linking can induce some thermosetting behaviors in PVAc structures and thus improve the performance of PVAc at elevated temperatures and humid conditions (Kaboorani and Riedl 2011b). These behaviors may be due to the reaction between the hydroxyl groups in the polymer molecular chain (such as urea formaldehyde resin and phenolic resin) and the hydroxyl or carboxyl groups in the PVAc molecular chain. These reactions can generate either an ether bond or an ester bond, which are both insoluble in water.

The purpose of this study was to design cheap and renewable membranes based on liquefied agricultural waste products, and to evaluate the properties of these membranes. For these reasons, experiments were carried out with the use of a liquefaction technique, in the presence of polyethylene glycol 400 and glycerin (4:1, w/w) as a liquefying reagent, with sulphuric acid as catalysts, under atmospheric pressure. Banana pseudo-stems were the raw materials that were used to produce the aforementioned polyols. The liquefied banana pseudo-stem (LBPS), without introducing an esterification process, blends with PVAc, allowing the prepared membrane to perform well in water. In this study the authors characterize the LBPS and evaluate the mechanical, structural investigations, thermal stability and cross-section morphologies of LBPS membranes mixing with PVAc, which will have potential to be applied in preparing high elongation leathers and resins.

EXPERIMENTAL

Materials

Banana pseudo-stem was collected from the campus of Hainan University, China. It was crushed into powder and sieved to 50 mesh (300 μm), dried at 105 °C for 24 h, and then stored in a desiccator at room temperature. Polyethylene glycol 400 (PEG400, chemical purity; Xilong Chemical Co., Ltd., China), glycerin (analytical reagent; Fanyuliqiang Chemical Co., Ltd., China), and sulfuric acid (98%) were used in these studies. Commercial polyvinyl acetate emulsion (PVAc) was purchased from the Zhejiang Haiyan Emulsion Coating Factory (China).

Preparation

A mixed solvent of PEG400 and glycerin (4:1, w/w), banana pseudo-stem powder, and quantitative sulfuric acid (98%) were added to a three-necked glass flask equipped with a stirrer, condenser, and thermometer. Liquefaction was carried out at 140 °C for 120 min. After the liquefaction, the whole dark brown mixture was cooled down and then diluted with ethyl alcohol. The resultant mixture was filtered through a Buchner funnel with a piece of medium speed quantitative filter paper (pore diameter 30 to 50 μm) to separate the residue and filtrate.

The residue was dried in an oven at 105 °C for at least 12 h to a constant weight and was used for the calculation of liquefaction yield. Liquefaction yield was determined by the following equation (Eq. 1).

$$\text{Liquefaction yield (\%)} = \left[1 - \frac{\text{weight of residue}}{\text{weight of raw material}} \right] \times 100\% \quad (1)$$

The ethyl alcohol in the filtrate was removed by rotary heating with steam. The resulting liquid fraction was called liquefied products of banana pseudo-stem (LBPS) and used for future study.

Liquefied banana pseudo-stem membranes were prepared with different LBPS/PVAc mass ratios (0, 1/10, 1/5, and 1/3, w/w). The mixtures were stirred for 30 min and then cast into glass sheets. The cast membranes were then dried at room temperature (at least 12 h) and 100 °C for 1.5, 2.5, and 3.5 h, respectively.

Methods

The average molecular weight (M_w) of LBPS components was performed by using a Waters 1515 chromatographic apparatus equipped with a Styragel HR-4THF column, using 0.1% THF solution as eluent, at a flow rate of 0.6 mL/min. The detection was done with a refractive index detector (Waters 2414).

The hydroxyl number of LBPS was determined and corrected according to Hassan and Shukry (2008)

The membranes were kept at 30 °C and a relative humidity of 80% for 7 days and were then cut into 100 mm × 10 mm long strips. The tensile strength, elongation, and tensile modulus of the membranes were obtained using a universal testing machine (WDW-1, Ji Nan; China). Five specimens (100 mm × 5 mm) were tested from each kind of membrane and the mean values were adopted. The performance of the membranes in water, such as water resistance and ductility, were observed after putting the specimens (10 mm × 10 mm) in water at room temperature for a week.

The FTIR-ATR analyses of the LBPS/PVAc membranes and pure PVAc were carried out using a Fourier transform infrared spectrophotometer (SENSOR27, Bruker Optics; Germany) equipped with a deuterated triglycine sulfate detector (DTGS) and a single reflection attenuated total reflectance (ATR) crystal accessory. Spectra were acquired in a range of 600 to 4000 cm^{-1} through the performance of 16 scans at 4 cm^{-1} resolution.

The thermal decomposition behavior of the membranes was studied using the NETZSCH5 209F3 thermogravimetric analyzer over a temperature range of 40 to 750 °C, at a heating rate of 10 °C/min under a nitrogen flow rate of 20 mL/min. To avoid unwanted oxidation, thermal atmosphere stability measurements were conducted with the samples placed in high quality nitrogen (99.999% pure) atmosphere.

To visualize the surface structure of membranes and the compatibility of LBPS and PVAc, fractured surfaces of the membranes coated with gold were examined using a Hitachi S3500N scanning electron microscope (Japan) operating at an accelerating voltage of 10 kV.

RESULTS AND DISCUSSION

Characteristics data of LBPS

Banana pseudo-stem is composed of cellulose (about 24.17%), hemicellulose (25.92%), and lignin (10.88%). In the liquefaction process, hemicellulose and lignin were the more susceptible components to liquefaction, followed by the cellulose, but lignin is easily condensed in the presence of acid after a certain reaction time (Zhang *et al.* 2014). It can be speculated that the LBPS is composed of hemicellulose, lignin, and cellulose derivatives. Characteristics of liquefaction and LBPS are shown in Table 1. It is apparent that the vast majority of banana pseudo-stem had dissolved, and the low-molecular-weight LBPS, which is rich in functional hydroxyl groups, was obtained by liquefaction. Furthermore, the LBPS is a kind of homogeneous solution that has good flow ability.

Table 1. Characteristics of Liquefaction and LBPS

Liquefaction yield (%)	Average molecular weight of LBPS(Mw)	Hydroxyl number of LBPS (mg KOH/ g)
81.78	737	298.50

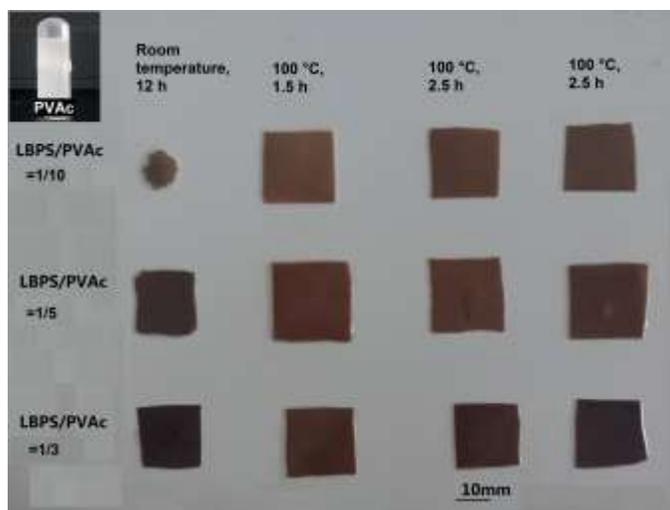
Mechanical Properties

Mechanical properties such as elongation, tensile strength, and tensile modulus of the LBPS/PVAc membranes were evaluated by tensile tests. Table 2 presents the details of these membrane tests under various conditions. As can be seen from the table, the addition of LBPS into PVAc was able to improve the elongation of PVAc membrane in spite of the mixture proportion. Comparing the elongation with samples that were prepared at room temperature, the maximum elongation at break of the blending membranes reached 779% when LBPS was added to PVAc membranes. Such inspiring results provide an effective method to prepare high elongation leathers and resins. Furthermore, the addition of LBPS into PVAc results in the reduction of the tensile strength and modulus under various reaction conditions, which is instructive in preparing joint sealing and cushioning materials.

Table 2. Mechanical Properties of LBPS/PVAc Membranes Prepared at Various Conditions

	Mass ratio of LBPS/PVAc	Elongation (%)	Tensile strength (MPa)	Tensile modulus (MPa)
Room temperature, 12 h	0	524.2	35.698	5.514
	1/10	730.7	24.296	2.392
	1/5	720.2	13.226	1.26
	1/3	779	14.642	1.422
100 °C, 1.5 h	0	459.5	27.09	4.67
	1/10	626.5	29.048	2.7525
	1/5	610.8	14.904	1.268
	1/3	559.4	10.246	0.808
100 °C, 2.5 h	0	446.8	29.95	5.424
	1/10	602.1	28.086	2.31
	1/5	624.3	15.53	1.224
	1/3	552	6.482	0.776
100 °C, 3.5 h	0	379.4	35.628	4.172
	1/10	553.3	24.192	2.076
	1/5	613.33	13.44	1.19
	1/3	554.2	6.978	0.844

The ductility and stability performance of PVAc membranes in water are greatly influenced by LBPS. There is always an expansion for LBPS/PVAc membranes after putting them into the water, which can be seen from Fig. 1. According to a simple area measurement, it can be found that the area of LBPS/PVAc membranes was able to expand to 2.5 times the size of the original membranes when the membranes were soaked for a week, indicating the hydrophilic and water-swellaable characteristics of the LBPS/PVAc membranes.

**Fig. 1.** Performance of LBPS/PVAc membranes in water (after a week)

Another significant feature of the LBPS/PVAc membranes is the stability in a water environment. It can be seen that the pure PVAc membrane had almost dissolved in water after soaking in water for a week, while membranes treated with LBPS remain undamaged.

In fact, the curing process of membrane consists of water evaporation and the subsequent formation of hydrogen bonds, both of which are vulnerable to water and elevated temperatures. With respect to the chemical structure, water-absorbent polymers usually have a proper crosslinking degree or a partially-crystalline structure, which make the materials insoluble in water. Adding LBPS to PVAc may limit the formation of hydrogen bonds and even trigger some cross-linking reactions between LBPS and PVAc thus improving the performance of membrane under humid conditions. Upon heating (100 °C), the crosslinking degree of LBPS/PVAc was increased. These results indicate that blending LBPS with PVAc is favorable not only to the mechanical properties but also to the water performance of membranes.

Fourier Transform Infrared (FTIR) Spectroscopy

To understand the functional mechanism of LBPS, components in these membranes were studied by FTIR analysis. Figure 2 presents the FTIR spectra ranging from 600 cm^{-1} to 2000 cm^{-1} of samples that were prepared at various conditions, including various ratios of LBPS/PVAc and preparation temperatures. With respect to the LBPS/PVAc membranes that were prepared at room temperature (lines B and C), the vibrational modes for esters that are located at 1735, 1238, and 1014 cm^{-1} were weakened, while the vibrational mode located at 1085 cm^{-1} , which is associated with ethers, became stronger as the LBPS content increased. These results indicate an increase of ethers and a reduction of esters in membranes treated with the addition of LBPS under room temperature conditions. The C-O-C groups can result in the enhancement of elongation due to the free-rotation capability.

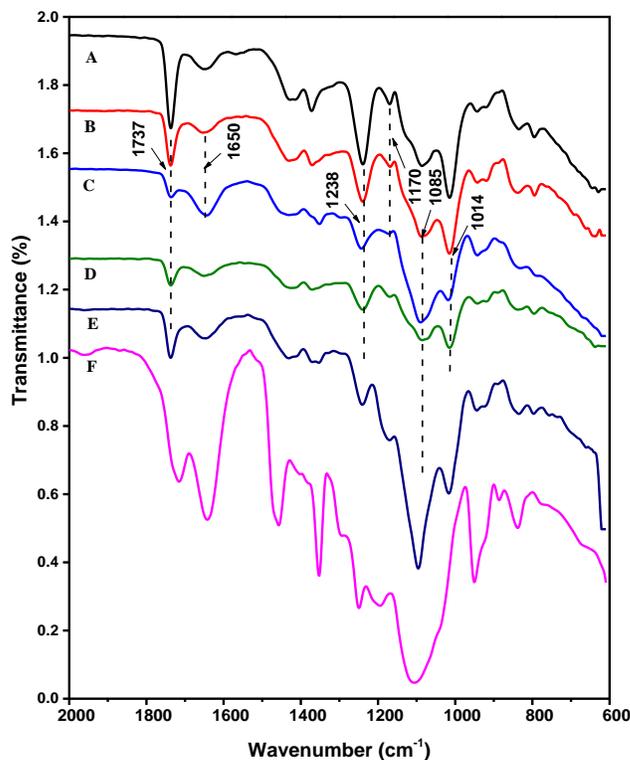


Fig. 2. FTIR spectra of LBPS/PVAc and PVAc membranes: (A) PVAc, room temperature; (B) LBPS/PVAc=1:10, room temperature; (C) LBPS/PVAc=1:3, room temperature; (D) LBPS/PVAc=1:10, 3.5 h, 100 °C; (E) LBPS/PVAc=1:3, 3.5 h, 100 °C; and (F) LBPS

Because hydrogen bonds are vulnerable to water and elevated temperatures, FTIR spectra of LBPS/PVAc membranes prepared at 100 °C exhibited a different reaction mode compared with the membranes prepared at room temperature. As the LBPS content increases, the increase of C-O-C along with the reduction of C=O in membranes becomes more evident. These results indicate that, at a high temperatures (100 °C), the crosslinking degree of LBPS/PVAc is increased. This increased crosslinking is due to the reaction between the hydroxyl groups in the LBPS and the hydroxyl groups in the PVAc, which restricts the free-rotation capability of the C-O-C groups.

Thermal Properties of PVAc Membranes

The LBPS/PVAc together with the pure PVAc membranes were characterized by TGA. It can be seen from Fig. 3 that the thermostability of PVAc membranes was greatly affected by both the preparation temperatures and the addition contents of LBPS. Firstly, with respect to the mass-loss pattern of pure PVAc membranes, the LBPS/PVAc membranes prepared at room temperature (Fig. 3a) exhibited a different mass-loss pattern than those prepared at 100 °C (Fig. 3b) when measurements were implemented below 250 °C. Secondly, it can be found that the additional content of LBPS in PVAc had a great impact on such thermostability when the testing temperature was changed from 250 to 300 °C. In this temperature range, the thermostability for all of the LBPS/PVAc membranes was less than that of the pure PVAc membranes. This situation became more evident with the increase of LBPS content due to the poor thermal stability of LBPS. Furthermore, when the temperature exceeded 300 °C, the thermostability of PVAc membrane was worse than that of LBPS/PVAc membranes due to the increase of C-O-C groups.

To further confirm the reaction mechanism of LBPS/PVAc compound, the differential TGA (DTG) plots are shown in Figs. 3c and 3d. The maximum weight-loss rate for pure PVAc membranes occurred at 269 °C, while that of LBPS/PVAc changed according to the preparation temperatures and the addition contents of LBPS. The maximum weight loss for LBPS/PVAc membranes that were prepared at room temperature occurred mainly at low temperatures (~230 °C). The intensity and area of the peaks were weaker than that of pure PVAc. However, the weight-loss peak at 433 °C was enhanced when LBPS was introduced into PVAc. Another set of LBPS/PVAc membranes that were prepared at 100 °C exhibited a similar trend.

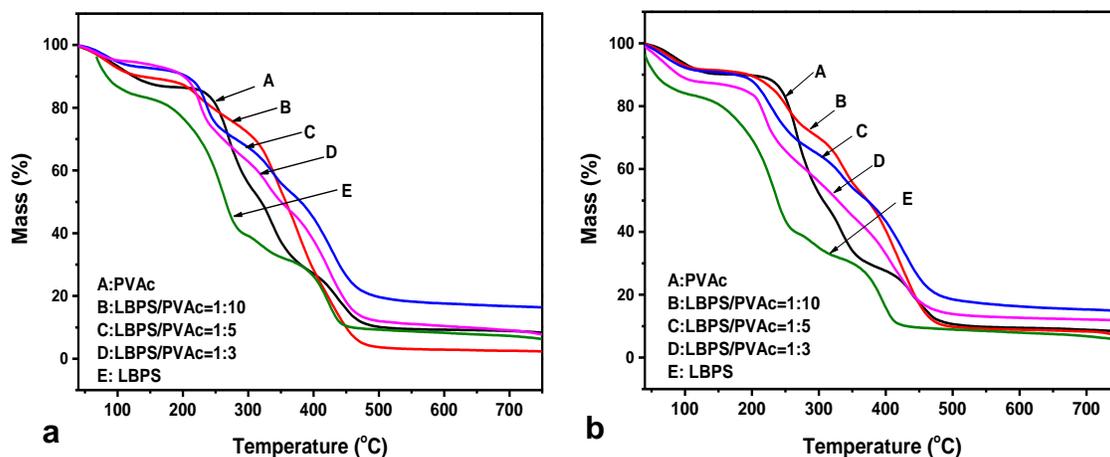


Fig. 3. Thermal stability of LBPS/PVAc and PVAc membranes (mass loss): (a) room temperature; and (b) 100 °C, 3.5 h

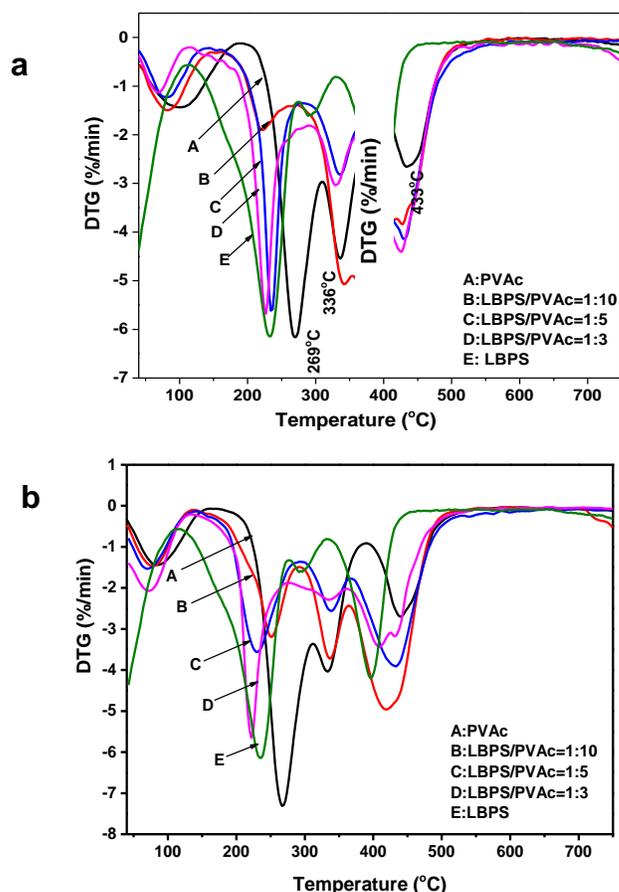


Fig. 4. Thermal stability of LBPS/PVAc and PVAc membranes (dM/dT curve): (a) room temperature; and (b) 100 °C, 3.5 h

Morphology Analysis

Figure 5 shows the fracture surfaces of LBPS/PVAc membranes representing blending with different LBPS contents. The sea-islands structure of pure PVAc membranes shown in Fig. 5a was materially changed in comparison to that of LBPS/PVAc membranes prepared at room temperature. When LBPS/PVAc was increased from 1/10 to 1/3 (Figs. 5b, 5c, and 5d), the density of the membranes gradually decreased and more irregular corrugation emerged on these rough fracture surfaces. The morphologies and features shown in the images may be consistent with an increased bonding between LBPS and PVAc, and the bonding may be due in part to hydrogen bonds. However, the addition of LBPS will limit the formation of intermolecular hydrogen bonds of PVAc, which would tend to become weaker when immersed in water. Such an irregular corrugation can account for the enhancement of elongation. Moreover, gaps can be seen from these fracture surfaces of LBPS/PVAc membranes, which further explain the mechanism of the hydroscopicity.

However, LBPS/PVAc membranes that were prepared at 100 °C exhibited different fracture characteristics. By comparison with the fracture surface of pure PVAc membranes shown in Fig. 6a, it can be seen that more folded-chain fringed micellar particles were formed when a small quantity of LBPS (LBPS/PVAc=1/10) was mixed into the membrane. In this regard, with an increase of LBPS/PVAc from 1/10 to 1/5 (Figs. 6b and 6c), no linear micelles were observed, but plenty of irregular particles joined together and tended to form a coherent phase.

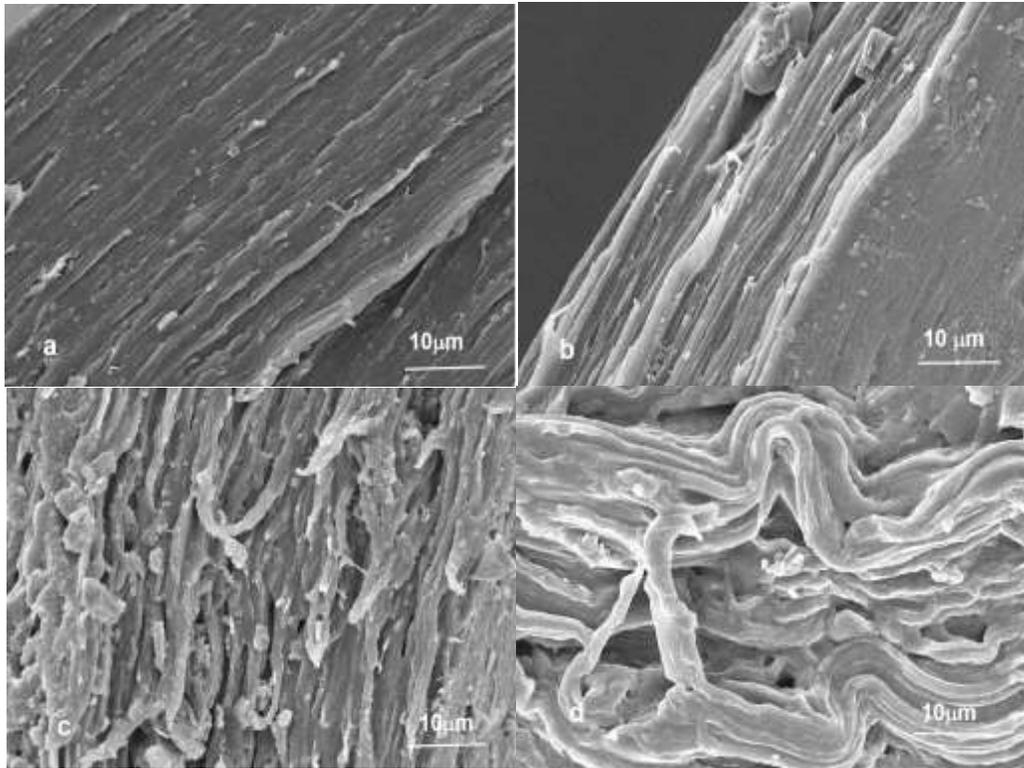


Fig. 5. SEM images of PVAc and PVAc/LBPS membranes: (a): PVAc; (b) LBPS/PVAc =1:10; (c) LBPS/PVAc =1:5; and (d) LBPS/PVAc =1:3

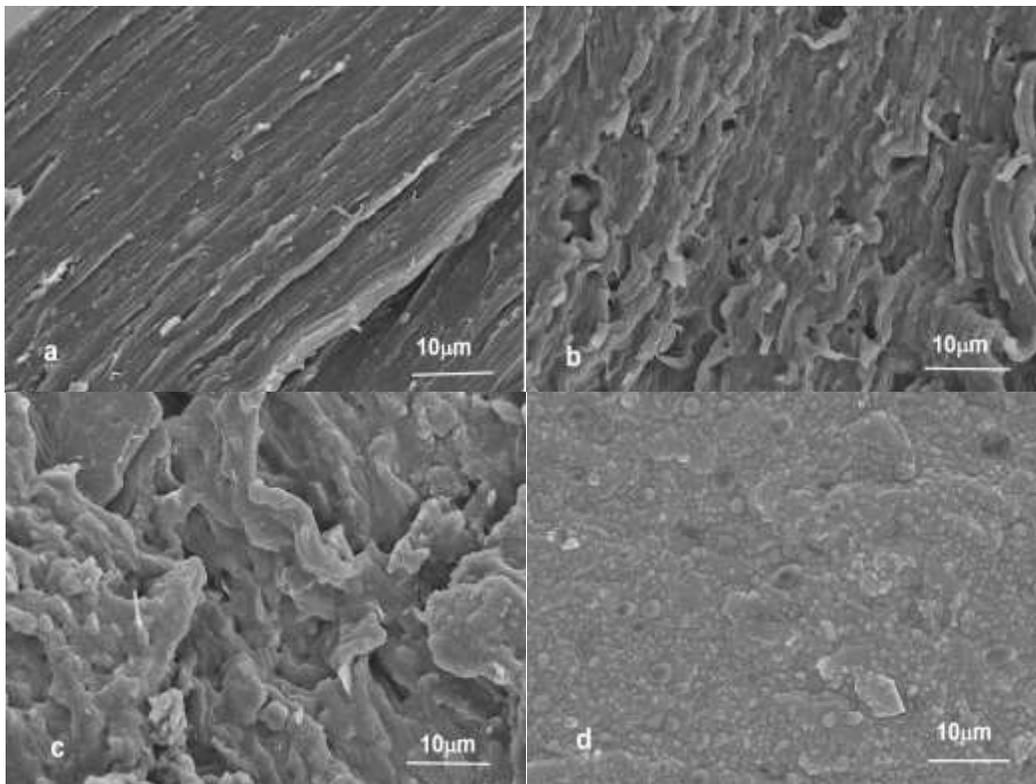


Fig. 6. SEM images of PVAc and PVAc/LBPS membranes: (a) PVAc; (b) LBPS/PVAc = 1:10, 100 °C, 3.5 h; (c) LBPS/PVAc = 1:5, 100 °C, 3.5 h; and (d) LBPS/PVAc = 1:3, 100 °C, 3.5 h

The fracture surface of LBPS/PVAc membrane shown in Fig. 6d is quite smooth, and plenty of particles can be observed. With such a special cross-linked structure at the fracture surface the water resistance of the materials can be improved.

CONCLUSIONS

1. A series of novel membrane materials were prepared based on liquefied banana pseudo-stem (LBPS) blending with different proportions of polyvinyl acetate emulsion (PVAc).
2. It was found that the enhancement of elongation and thermostability for the prepared membranes is due to the increase of C-O-C groups.
3. It was noteworthy that the blending membranes prepared at 100 °C can survive in water for a long time, and part of them can even expand to three times the size as the pure PVAc membranes without being destroyed.
4. The liquefied banana pseudo-stem is found to be a potential biobased polyols. These synthetic materials have the potential to be applied in the preparation of high-elongation leathers and resins.

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