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Morphology Control and Advanced Properties of Bio-Aerogels from Pineapple Leaf Waste

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Pineapple has been known as one of the most popular tropical fruits in Vietnam with a production of over 674,000 t in 2018. However, by-products from pineapple cultivation account for approximately 65 % of the fresh fruit weight and are mostly being dumped, decomposed or burnt now. Therefore, it has recently raised great concern about environmental pollution. For the first time, extracted fibres from pineapple leaves being utilized for developing successfully eco-friendly and cost-effective pineapple fibres (PFs) aerogels by using polyvinyl alcohol as a cross-linker and following a freeze-drying method. The morphology of the PFs aerogels can be controlled well by changing the PFs concentration (0.5 - 2.0 wt%). The PFs aerogels exhibit extremely low densities (12.7 - 32.6 kg/m^3) and high porosities (96.9 - 98.8 %). The BET result shows that the surface area of the PFs aerogel has up to 5.6 m^2/g and their pore size of 1.3 - 2.2 nm. The developed PFs aerogels show extremely low thermal conductivities ranging from 0.030 to 0.034 W/m.K. Due to the low Young's modulus values ranging from 0.47 - 7.86 kPa, the PFs aerogels are flexible and can be used for heat insulation of the buildings as well as food preservation.

1. Introduction

Agriculture is a crucial sector which was contributed 8.7 % to the overall growth of the Vietnamese economy in 2018. Pineapple has been known as one of the most popular tropical fruits in Vietnam with a production of over 674,000 t in 2018 (General Statistics Office, 2018). Currently, the pineapple fruits are the main commercial products of pineapple production. And the rest of the pineapple plant (stems, roots and especially leaves) are considered agricultural residues of pineapple cultivation. (Roni et al., 2013). Moreover, the by-products from the pineapple cultivation after fruit harvest account for approximately 90 - 150 t per hectare (Liu et al., 2013). They are mostly burnt in situ, dumped, decomposed or just crammed to rot (Roni et al., 2013). When pineapple plant waste left in a landfill to be decomposed or burnt, a large amount of toxic carbon dioxide, carbon monoxide, methane, volatile organic compounds, nitrogen oxides and halogen compounds are released and cause the environment hazards (Tripathi et al., 2013). Therefore, it is essential that the pineapple plant waste can be converted into useful high-value products, instead of disposing them as a waste. The PFs are the by-product from the pineapple cultivation. The major chemical composition of the PFs consists of cellulose (75 %), hemicellulose (16 %) and lignin (9 %) (Norazreen et al., 2018). Because of the high biodegradable cellulose content, the PFs can be recycled for various applications such as paper (Yusof et al., 2012), textile industry (Dipshika et al., 2017), food packaging (Sasikala and Umapathy, 2018), acoustic barrier (Girish et al., 2018), medical applications (Kengkhetkit and Amornsakchai, 2012), automotive and electrical applications (Ramnath et al., 2014), polymer composites (Sanjay et al., 2017) and co-composting (Hoang et al., 2019). In comparison with other natural fibres, Young's modulus of the PFs show the highest property (Asim et al., 2015). So the PFs can improve structural material once the PFs are converted into a

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new aerogel material. In this paper, strong silky fibres are extracted from pineapple long leaves and whole PFs fibres are used for fabrication of bio-aerogel.
Aerogels are an exciting solid material that are known for their extreme low density (0.003–0.500 kg/m^3), high porosity (80.0 - 99.8 %), large specific surface area (100 – 1,600 m^2/g) (Long et al., 2018). Due to its excellent properties, the aerogels can be used for the above-mentioned engineering applications. Over the past decades, synthesis methods for manufacturing biocompatible cellulose-based aerogels using recycled cellulose fibers of paper (Son et al., 2013), cotton waste (Hanlin et al., 2017), banana peel (Xuejie et al., 2018) and Kymene cross-linkers have been developed. However, there are no studies of recycling pineapple leaves waste into advanced PFs aerogels. In this paper, the biodegradable PFs aerogels from the pineapple plant waste are successfully developed using the cost-effective freeze-drying method for the first time. Besides that, the non-toxic solvents and chemicals are used in this eco-friendly fabrication method. The structures, the thermal conductivity and mechanical properties of the PFs aerogels are investigated comprehensively. The developed PFs aerogels can be the potential candidate for several applications such as heat insulation of the buildings as well as food preservation.

2. Materials and method

2.1 Materials

Polyvinyl alcohol (PVA) (MW: 70,000 to 120,000) is purchased from Sigma-Aldrich. The pineapple fibres (PFs) which extracted from pineapple fibres leaves are obtained from the commercial market with a length of 60 cm. The PVA flakes and PFs are used as purchased without further purification. Deionized (DI) water is used throughout the experimentation.

2.2 Fabrication of the PFs aerogels

Extraction of fibres from pineapple leaves is carried out by mechanical processes. The waxy layers of pineapple leaves are removed to obtain the PFs (Figure1). For fabrication of PFs aerogels, first, the PFs are blended for 5 min using a blender to cut the long PFs into smaller ones (0.3 - 1.5 mm) for improving the PFs dispersion. The various PFs concentrations of 0.5, 1.0, and 2.0 wt% and 0.2 g of PVA are added into 100 ml of DI water and then mixed in a cylindrical plastic mould. The obtained suspension is sonicated by a probe sonicator (Hielscher Ultrasonic Homogenizer UIP2000hdT) at 200 W for 10 min to enhances its homogeneity. The obtained mixture is then cured at 80 °C for 2 h for physical crosslink interaction between PVA and hydroxyl groups on the surface of the PFs. After curing, the PFs aerogel sample is frozen at -18 °C for 24 h by using a freezer in order to form a gel network in the ice with the PFs. Then, the frozen mould is freeze-dried using a freeze dryer (Toption TPV-50F Vacuum Freezer Dryer) (Figure 2).

(a) (b) (c)

Figure 1: Manufacture of PFs with (a) pineapple cultivation (Asim et al., 2015), (b) extraction of fibres from pineapple leaves and (c) PFs.

Freeze drying is required to deactivate the hydrogen bonding present in water which, due to cohesive forces, would otherwise cause the structure to collapse if it was dried in liquid state at ambient conditions. Based on the previous researches of our lab, the PFs aerogel morphology is only affected dramatically by the changes of PFs concentration. The various PFs concentrations of 0.5, 1.0, and 2.0 wt% are investigated and summarized in Table 1.

Table 1: The various compositions of the PFs aerogels

	Pineapple fibres (wt%)	PVA (wt%)	Density (kg/m^3)	Porosity (%)	Young's modulus (kPa)
0.5 wt% PFs	0.5	0.2	12.72	98.85	0.47
1.0 wt% PFs	1.0	0.2	21.02	98.07	4.63
2.0 wt% PFs	2.0	0.2	32.63	96.98	7.86

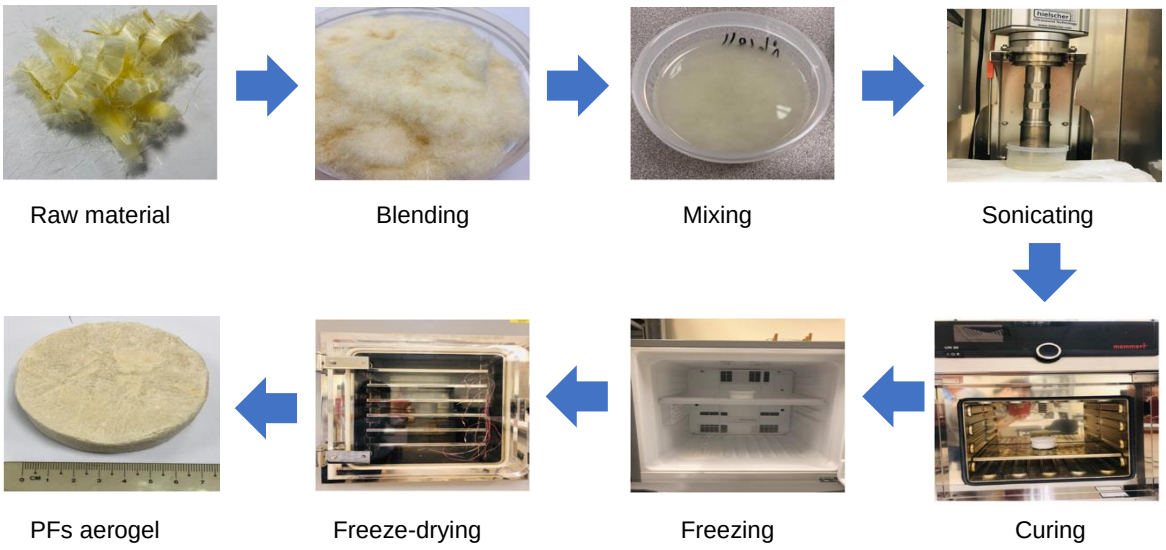


Figure 2: Fabrication steps of the PFs aerogel from the PFs of the pineapple leaves.

2.3 Characterization

In order to determine the specific surface areas and pore size of the PFs aerogels samples, Brunauer Emmett Teller (BET) and Barrett Joyner Halenda (BJH) methods were used. All samples were degassed at 80 °C in vacuum for 24 h before measurement (Son et al., 2012).
The density of the aerogels (ρPFs aerogels) was then calculated using Eq(1):

$$\rho_{PFs\ aerogels} = \frac{m_{PFs\ aerogels}}{V_{PFs\ aerogels}} \quad (1)$$

Where m is mass of PFs aerogels, V is the volume of PFs aerogels.
The average density of PFs and PVA (ρ_a) of the aerogels was then calculated using Eq(2):

$$\rho_a = \frac{C_{PFs\ aerogels} + C_{PVA}}{\frac{C_{PFs\ aerogels}}{\rho_{PFs\ aerogels}} + \frac{C_{PVA}}{\rho_{PVA}}} \quad (2)$$

Where C is concentration in weight percentage, ρ is density.
The density of the aerogels was then calculated using Eq(3) (Feng et al., 2015):

$$\text{Porosity, } \emptyset = \left(1 - \frac{\rho_{PFs\ aerogels}}{\rho_a}\right) \times 100\% \quad (3)$$

where: ρ is density, m is mass, V is volume, and C is a concentration in weight percentage.
To investigated the morphology and microstructure of PFs aerogels, the samples were coated with a thin layer of gold at current of 20 mA for 30 s using a sputtering machine (Cressington Sputter Coated 108 Auto) and then placed under a field-emission scanning electron microscope (FE-SEM, Model S- 4300 Hitachi, Japan) (Jingduo et al., 2016).
The thermal conductivity, also known as K value, of the PFs aerogels was measured using the C-Therm TCi Thermal Conductivity Analyzer (C-Therm Technologies, Canada). The equipment using the Modified Transient Plane Source (MTPS) technique where a one-sided interfacial heat reflectance sensor will constantly apply

heat onto the aerogels. The higher the K value, the better it is at conducting heat. *Three times an experiment* is *repeated* for each PFs aerogel sample and an average value was taken.
The mechanical properties of the aerogels were carried out on an Instron 5,500 micrometer (USA) to determine the compressive modulus of the PFs aerogels. During the test, the aerogels were compressed at a load rate of 1 mm/min using a 1,000 N load cell.

3. Results and discussion

3.1 Morphology and structure of the PFs aerogels

Figure 3 presents the developed aerogels exhibit the extremely low densities (12.7 - 32.6 kg/m^3) and high porosities (96.98 – 98.80 %), which indicates the light weight and the porous structures of the PFs aerogels. The PFs aerogel has the denser network and the less porosity when increasing the PFs concentration. It can be explained that larger PFs concentrations in the initial solution can take up more space in the PFs aerogels. Also more cross-linking bonding formed can cause more packed and have less air pockets in the PFs aerogel network as shown in Figure 3. The surface area and total pore size values range 3.7-5.6 m^2/g and 1.3 - 2.2 nm.

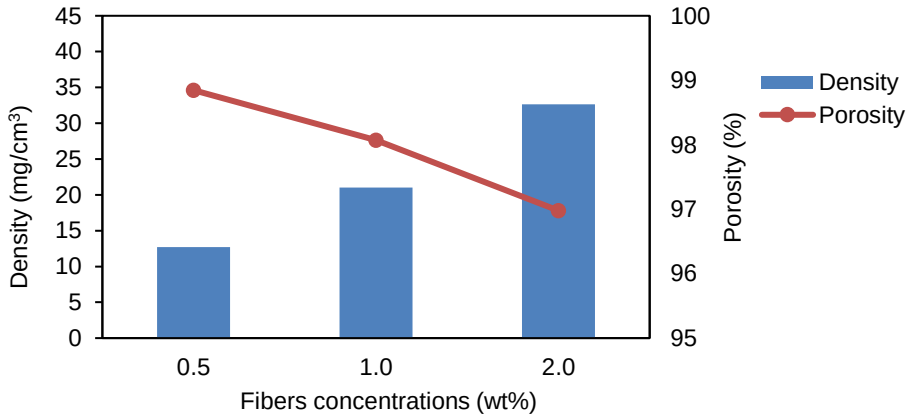
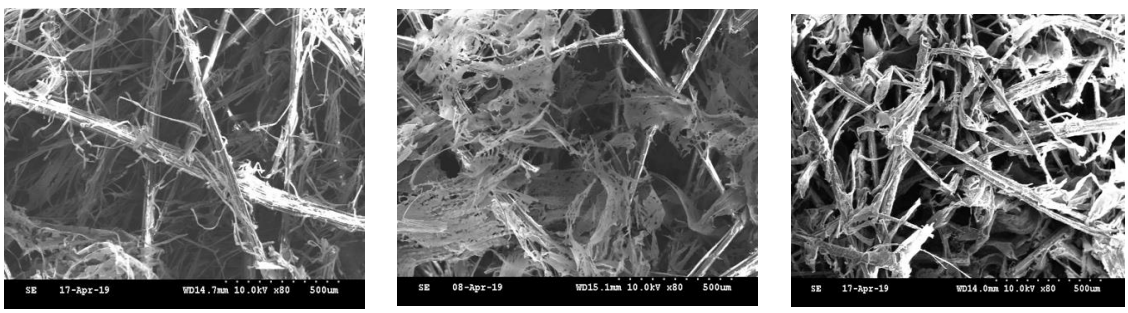


Figure 3: Morphologies of the PFs aerogels with the different PFs concentrations

To determine the morphology of PF aerogel, its SEM images were captured. As depicted in Figure 4, when a higher concentration of fibres is used, the aerogels become more closely packed and there are lesser air pockets within them, indicating an increase in density and decrease in porosity. This is consistent with the trend observed in Section 3.1. Because most of the hydroxyl groups in cellulose molecules have already formed either intra- or inter-molecular hydrogen bonds within each other and both PFs and PVA are rather hydrophilic, the formation mechanism them is generally considered to involve the formation of physical cross-linking points through intra- and intermolecular hydrogen bonding interactions between polymer chains during the pre-gelation stage. At low cellulose concentration, the new added cellulose mainly formed intermolecular interactions between the cellulose and PVA molecules and replaced the original interactions between the PVA molecules.



(a) (b) (c)

Figure 4: FE-SEM images of the PFs aerogels having (a) 0.5 wt%, (b) 1.0 wt% and (c) 2.0 wt% of the PFs.

3.2 Thermal conductivities of the PFs aerogels

Figure 5 shows the thermal conductivities of the synthesized PFs aerogels are extremely low (0.030 – 0.034 W/m.K). This can be explained by the highly porous PFs aerogel structures made up of over 95 percent air by weight. And air also a good heat insulator with K_{air} = 0.026 W/m.K at room temperature (Wen and Nyan, 2008). When increasing fibres concentration, the thermal conductivity of the PFs aerogel increases. It can be explained by its denser structure with more PFs having a larger value of K_{PFs} = 0.21 W/m.K (Ravindra et al., 2003).

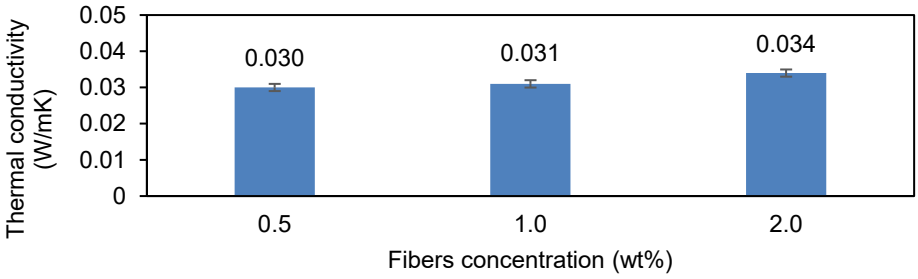


Figure 5: Thermal conductivities of the PFs aerogels with different PFs concentrations.

3.3 Mechanical property

The mechanical properties of the PFs aerogels also play a vital role in the thermal and insulation applications. Therefore, compressive tests of the PFs aerogel samples are carried out in this study. As shown in Table 1, Young's modulus of the PFs aerogels increases when the PFs content increases from 0.5 to 1.0 and 2.0 wt%. This can be explained that the larger PFs concentration leads to reinforcing the gel structure formed during gelation. Moreover, the PFs aerogels have a very low Young's modulus (0.47 – 7.86 kPa) compared to other cellulose aerogels (13 - 39 kPa) (Nguyen et al., 2014) or silica-cellulose hybrid aerogels (86 – 169 kPa) (Jingduo et al., 2016), which shows that they can be flexible and elastic as shown in Figure 6.

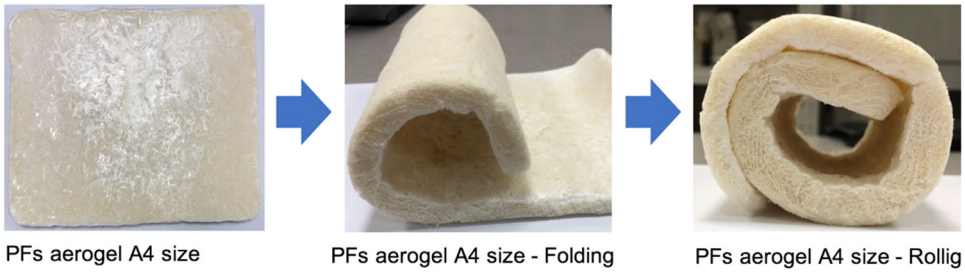


Figure 6: Good flexibility of developed PFs aerogels from the PFs.

4. Conclusions

In this study, for the first time, the novel PFs aerogels are successfully synthesized using the non-toxic cross-linker and the cost-effective freeze-drying method. The PFs aerogel morphology depends much on the PFs content. The thermal and mechanical properties can be enhanced by increasing the fibres content in the PFs aerogels. Effects of the PVA concentrations and using the PFs aerogels for the food preservation application will be investigated in future work.

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