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Microfibrillated Cellulose from Pineapple Leaves for Synthesizing Novel Thermal Insulation Aerogels

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Aerogels from cellulose and its derivatives, especially cellulosic wastes, have been known as an excellent heat insulation material in steam generation, buildings, intelligent food packaging, fire-retardant clothing, and thermal protective equipment because of their lightweight properties, high stability, and extremely low thermal conductivities. Towards the scope of maximizing the bio-based resources utilization in day-to-day life, pineapple leaves (PLs) are converted into microfibrillated cellulose (MFC) fibers. PLs are first pretreated step by step with NaOH and NaOH/H_2O_2 solution to enrich cellulose content. This was followed by acid hydrolysis (H_2SO_4 40 wt%) and high-speed homogenization for MFC production. The obtained cellulose microfibers are further exploited to produce cost-effective, eco-friendly, and high-value engineering aerogels cross-linked by a common polyamide amine-epichlorohydrin (PAE) for the first time. The developed procedure is feasibly applied to mass production at a pilot-scale because of its simplicity, cost-effectiveness, and environmental friendliness. The resulting aerogels exhibit ultra-low density (below 30.0 g/cm^3) and high porosity (above 98.0 %) along with high elasticity. Morphology analysis reveals that most of the pores within the aerogels are macroporous, and the diameter of fibers is around 2-3 μm. The heat conductivity of as-fabricated aerogels is in the range of 0.035-0.043 W/m·K, which is comparable to some heat insulation products such as glass wool (0.031-0.043 W/m·K), cellular glass (0.038-0.043 W/m·K), and mineral wool (0.034-0.045 W/m·K). The effects of cellulose and PAE contents on the morphology, physical, mechanical, and thermal behaviors of the synthesized aerogels are also investigated. The MFC aerogels from pineapple leaves are considered novel and promising candidates for bio-based heat insulation applications.

1. Introduction

At present, the increase in energy consumption, which contributes to over 30 % of greenhouse gas emissions, is negatively influencing the ecosystem (Jelle et al., 2015). Thermal insulation materials are now being studied with advanced properties to reduce energy consumption. Especially, aerogels are considered one of the most potential thermal insulation materials. Because of outstanding properties such as ultra-low density between 0.007 and 0.011 g/cm^3 (Thai et al., 2020), high porosity up to 99 %, and very low thermal conductivity ranging from 0.018 to 0.075 W/m·K (Long et al., 2018), aerogel exhibits noticeable characteristics compared to traditional thermal insulation materials. From that, aerogels are synthesized from cellulose, an abundant natural source, obtaining special features of aerogel and different extraordinary properties such as biodegradability, biocompatibility, and being easily functionalized for various purposes.
Recently, nanocellulose aerogel has made a significant impression because of its excellent performance, such as ultralight properties with a low density of 0.004-0.105 g/cm^3, a porosity of 92.8-99.9 %, large surface area of 10.9-892.0 m^2/g, and heat insulation (0.016-0.022 W/m·K) (Chen et al., 2021). With outstanding features,

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nanocellulose aerogel is researched to develop and improve various characteristics. Specifically, nanocellulose aerogels from pine trees were manufactured by Gupta et al. by using a sol-gel method on the nanocellulose obtained from the wood powders after the acidic hydrolysis. The heat conductivity of the fabricated aerogel is 0.026 W/m·K. Nonetheless, the process requires a high-intensity ultrasonicator (Gupta et al., 2018), which is one of the various complex types of equipment in this research. In addition, Lei Yang et al. synthesized cellulose nanofiber having functional groups from softwood pulp via oxidation using 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO), and enhanced thermal insulation of nanocellulose aerogel by mixing it with MoS_2 as a cross-linker (Yang et al., 2017). The synthesized aerogel has a thermal conductivity of 0.028 W/m·K, but TEMPO has a negative environmental impact, and the synthesis process is highly complicated.

Significantly, microfibrillated cellulose (MFC), the robust nanoscale building blocks, made by disintergrating cellulose (Zhou et al., 2015). MFC has illustrated the ability to form a highly entangled network characterized by high mechanical properties, which is important to obtain lightweight and flexible aerogels because of its high stiffness, high aspect ratio, and numerous hydrogen bonds (Sehaqui et al., 2009), while the synthesis process of MFC is more simplifying than that of nanocellulose. Specifically, Zhou et al. prepared MFC aerogels with an ultralow density of below 0.005 g/cm^3, high lipophilicity, and superior porosity of over 99.68 %, from softwood kraft pulp by using TEMPO as an oxidation factor (Zhou et al., 2016). Nevertheless, the synthesis processes of microfibrillated cellulose aerogels still encounter various difficulties in process design, high production cost, and being environmentally unfriendly due to using TEMPO.

Pineapple trees are one of the most growing trees in Vietnam with a total production capacity of 737.3 thousand tons in 2021 (Vietnam GSO, 2022). After each harvesting pineapple fruits, farmers spend a lot of money on processing the discarded leaves, stems, and roots of the pineapple plant by using herbicides or burning them, which mainly contributes to global warming. On the other hand, pineapple leaves (PL) with a great proportion of cellulose (36.3 ± 3.8 %) are potential to produce highly valuable products like nanocellulose aerogels (Nguyen et al., 2021).

To deal with those difficulties, in this paper, MFC was synthesized for the first time from pineapple leaves by combining medium concentration acidic hydrolysis and homogenization. The fabricated cellulose was then used to synthesize aerogels using polyamide amine-epichlorohydrin (PAE) as a cross-linker and freeze-drying. Furthermore, PAE is a common thermosetting polymer in paper manufactory with various active groups such as azetidinium and alkyl functional groups, which provides both chemical and physical cross-linking points for cellulose chains (Yang et al., 2017). The effect of PAE proportion on structure, crystal components, and thermal behaviors of aerogels was comprehensively investigated by advanced methods.

2. Experimental

2.1 Materials

Pineapple leaf (PL) fibers were collected after harvesting in Nghe An province, Vietnam. The fibers have a total cellulose content of 60.6 ± 2.0 %. Sodium hydroxide (NaOH, purity 96.0 %), and ethanol (C_2H_5OH, purity 99.5 %) were purchased from Xilong Scientific Co., Ltd, China. PAE from Shandong Bluesun Chemicals Co., Ltd, China. All experiments were conducted with reverse osm (RO water).

2.2 Preparation of MFC

Raw pineapple leaves were grounded to powders, then pretreated with NaOH 3 wt% at a liquid-to-solid ratio of 20:1 (w/w) for 2 h, at 80 °C for hemicellulose elimination. The obtained slurry was rinsed with RO water to pH 7. This process was repeated 3 times. Afterward, the system was then treated with a mixture of 10 wt% H_2O_2/1 wt% NaOH solution and 20:1 of liquid-to-solid mass ratio, at 80 °C for 1 h. The obtained powder was washed with RO water until pH-balanced before at 80 °C overnight. The acidic hydrolysis step was conducted with 40 wt% H_2SO_4 at 45 °C for 3 h and then terminated by adding water. The suspension was settled down over time and the supernatant was then removed before introducing fresh RO water into the residue. This process was conducted periodically until the suspension reached neutral pH. After that, the entire mixture was homogenized for 2 h at 15000 rpm to finally achieve the MFC suspension.

2.3 Fabrication of MFC aerogel

An aqueous suspension of 50 g cellulose fibers (1 wt%) and PAE (20-80 wt% of dry cellulose fibers) was vigorously agitated for 15 min. The suspension was then poured into a stainless-steel mold. Next, the sample is frozen in liquid nitrogen to obtain the hardened form, followed by freeze-dried by Toption TPV-50F lyophilizer under vacuum conditions for 48 h. Finally, the MFC aerogel was kept at 120 °C for 3 h to strengthen the aerogel structure by covalent bonds.

2.4 Characterization

The density of each MFC aerogel is calculated as its mass-to–volume ratio. The porosity (φ) is determined using thedensity (ρ_a) and the mean skeletal density of ingredients (ρ_b) as shown in Eq(1):

$$\varphi = \left(1 - \frac{\rho_a}{\rho_b}\right) \times 100\ \% \quad (1)$$

The average skeletal density ρ_b of the cellulose composite was calculated based on Eq(2):

$$\rho_b = \frac{1}{\frac{W_{Cellulose}}{\rho_{Cellulose}} + \frac{W_{PAE}}{\rho_{PAE}}} \quad (2)$$

where $W_{Cellulose}$ and W_{PAE} are the weight fraction of cellulose and PAE in the order given. The skeletal density of PAE (ρ_{PAE}) is assumed as 1.150 mg/cm^3, whilst that of cellulose ($\rho_{Cellulose}$) is assumed as 1.6 mg/cm^3 (Dilamian and Noroozi, 2021).

Scanning Electron Microscope (SEM, Hitachi S4800) was used to analyze the morphologies of the MFC aerogels. Before measurement, a thin film of Pt was coated on the samples. Fourier Transform Infrared spectrometer (FTIR) Bruker Alpha II equipment (USA) was utilized to determine the chemical structures of the MFC and MFC aerogels with the scanned range from 4000 to 500 cm^{-1}. The thermal stability of MFC aerogels was assessed using a thermalgravimetric analyzer (TGA, LINSEIS DSC PT 1600). The sample's temperature increased from ambient temperature to 700 °C at a constant rate of 5 °C /min. The heat conductivities of PF aerogels were examined using the HFM-100 Heat Flow Meter (Thermtest Inc., Canada) at ambient temperature. Three times each sample was tested, and an average value was determined.

3. Results and discussion

3.1 Morphology of MFC aerogels

Figure 1 gives information about the structure of MFC aerogels. The raw pineapple leaf fibers are 10-30 µm in diameter and 3,000-5,000 µm in length. After mild acidic hydrolysis and homogenization, there is a dramatic reduction in diameter to 2-3 µm and 20-40 µm in length. The aerogels are porous and have interconnected three-dimensional structures with a pore size of around 10-30 µm. Cellulose microfibers are linked by thin films of PAE via strong hydrogen bonds. In addition, as the PAE content rises, the aerogels become denser and fewer macropores could be observed. This also means that the structure goes strength since there are more hydrogen bonds within the aerogel. In general, there was a shrinkage of 30-60 v% after sublimation but the obtained aerogels were extremely light.

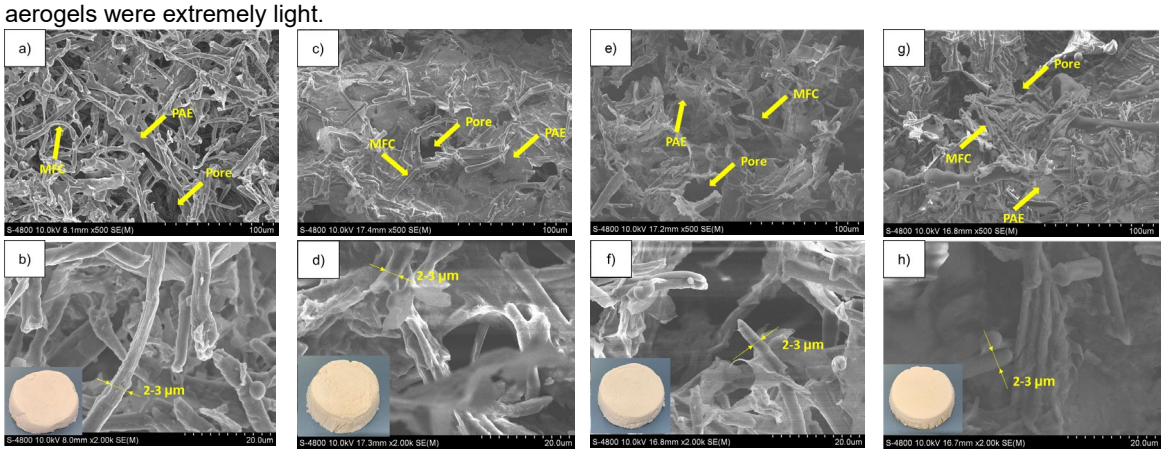

Figure 1: Effect of varing PAE content on the morphology of MFC aerogels: (a,b) 20 wt%, (c,d) 40 wt%, (e,f) 60 wt% and (g,h) 80 wt%

3.2 Density and porosity of MFC aerogels

Figure 2 illustrates how PAE content influences the bulk density and porosity of MFC aerogels. It could be seen that when the mass proportion of PAE grows up from 20 wt% to 80 wt%, the density rises steadily from 16.6 to 29.2 mg/cm^3, and the porosity goes down from 98.9 to 98.0 %. It is due to the denser structural feature of the material with the increasing solid concentration. Because of being fabricated from MFC, the aerogels are ultralight and much lighter than other cellulose aerogels such as the pineapple leaf aerogels (Do et al., 2020)

and the coconut coir fiber aerogels (Phuong et al., 2021) which were both fabricated by using polyvinyl alcohol as a cross-linker.

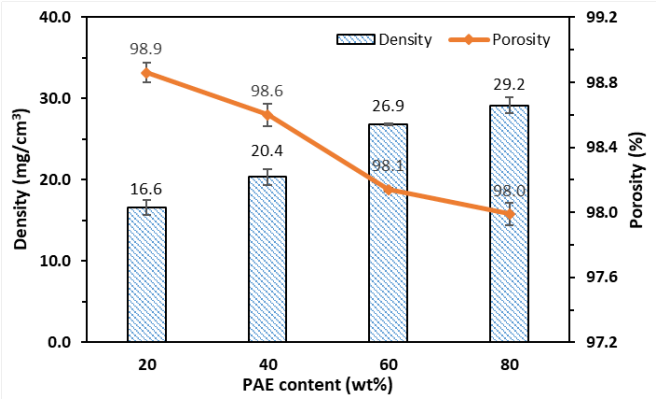

Figure 2: Density and porosity of MFC aerogels with increasing PAE content

3.3 Chemical structure of MFC aerogels

Figure 3 shows FTIR spectra of raw pineapple leaf pulp, pineapple leaf pulp after bleaching and acid pyrolyzing, and MFC aerogel cross-linked by PAE. Peaks at 3350 cm^{-1}, 2910 cm^{-1}, 1430 cm^{-1}, 1060 cm^{-1}, and 895 cm^{-1} associate with O-H stretching, C-H stretching, C-H bending, C-O-C skeletal vibration, and β-glycosidic linkage in that order (Do et al., 2022). In the raw material, there are some peaks at 1745 cm^{-1} (C=O stretching), 1508 cm^{-1} (C=C-C aromatic ring stretching and vibration), and 1235 cm^{-1} (C=O stretching of guaiacyl unit) in lignin and hemicellulose (Zhuang et al., 2020). After bleaching and acid pyrolyzing, these peaks were almost eliminated, proving that a great deal of lignin and hemicellulose was removed out of pineapple pulp and there was an increase in the cellulose content. A fresh peak at 1550 cm^{-1} attributing to the N-H bending of amide II appears in MFC aerogel which indicates the interaction between PAE and MFC (Dilamian and Noroozi, 2021).

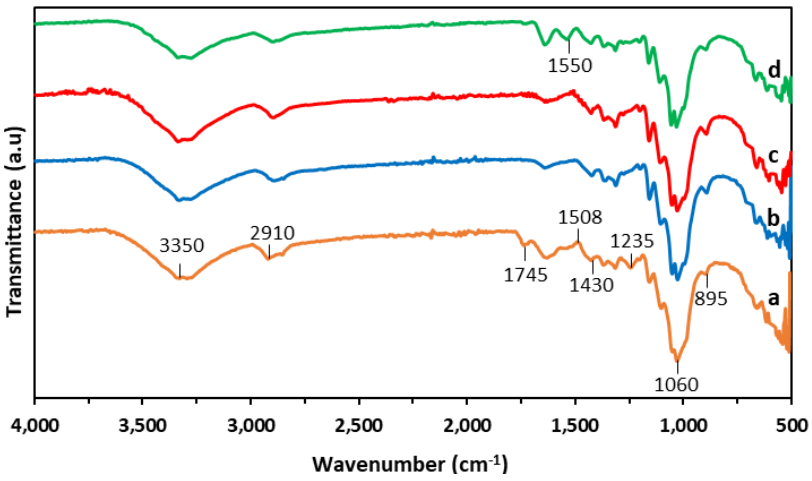

Figure 3: FTIR spectra of the (a) raw cellulose, (b) bleached cellulose, (c) MFC, and (d) MFC aerogel with 80 % of PAE

3.4 Thermal insulation characteristics of MFC aerogels

Heat conductivities of the MFC aerogels at different PAE contents are given in Figure 4. Overall, the heat conductivity of highly porous aerogels is around 0.037-0.041 W/m·K which is as low as other commercial building insulation materials such as glass wool (0.031-0.043 W/m·K), cellular glass (0.038-0.043 W/m·K), and mineral wool (0.034-0.045 W/m·K). Particularly, their heat conductivity could be 10 % lower than that of the previous pineapple leaf/cotton leaf aerogel composite (0.041 W/m·K) at the same solid concentration (Do et al., 2021). In addition, the thermal conductivity tends to decrease as the PAE content goes up. Undoubtedly, the thermal conductivity is a function of many factors such as cellulose and PAE thermal characteristics and their interactions, the porousness, and the dimension of poreswith in the material (Long et al., 2018).

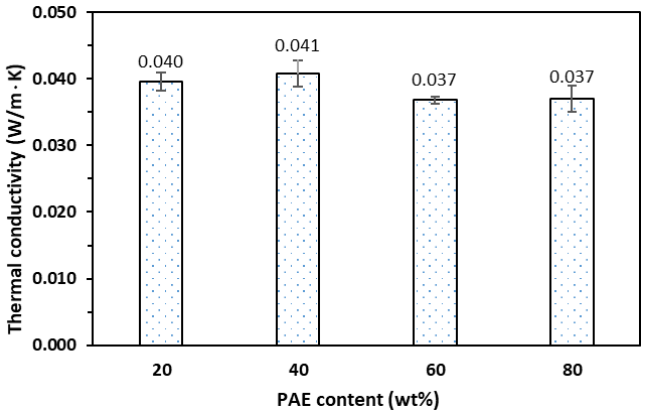

Figure 4: Heat conductivity of MFC aerogels with increasing PAE content.

3.5 Thermal stability of MFC aerogels

The TGA curves in Figure 5 show the thermal behavior of the MFC aerogel. There is a slight decrease in the weight of aerogel by approximately 4 % from room temperature to 60 °C since moisture and volatile compounds evaporated. More importantly, the mass of the aerogels keeps unchanged from 60 to 200 °C, this recommends that the maximum working temperature of the aerogels could get up to 200°C. The rapid mass loss process takes place from 250 °C to 350 °C due to the decomposition of MFC and PAE. There is almost no change in the weight of aerogel when the temperature gets to 500 °C, with the sample residue mass of around 15-17 %. Furthermore, as the PAE content increases, the thermal stability of the sample slightly decreases. This could be explained by the lower decomposition temperature of neat PAE than neat cellulose (Guo et al., 2018).

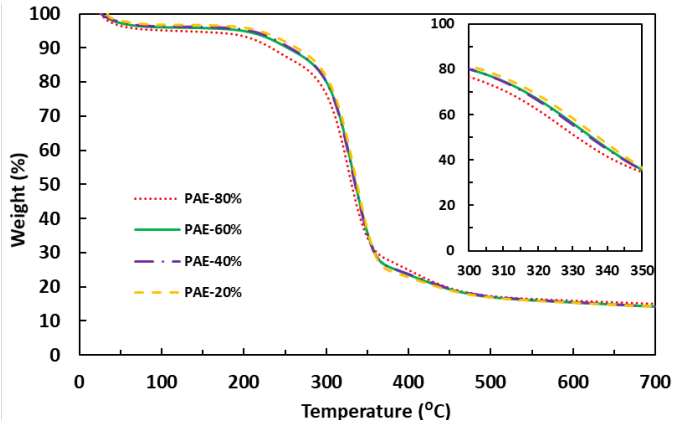

Figure 5: Thermal stability of the MFC aerogel composed of 1.0 wt% MFC at different PAE contents

4. Conclusions

MFC fibers with a diameter of around 2-3 μm were successfully generated from discarded pineapple leaves by combining acid hydrolysis in a milder condition and homogenizing. The resulted MFC fibers were then utilized to produce MFC aerogels cross-linked by PAE by simple mixing and cost-effective lyophilizing. The as-prepared aerogels expressed an ultra-low density of 16.6-29.2 mg/cm^3 and quite high porosity of above 98 %. Strikingly, the low thermal conductivity of around 0.037-0.041 W/m·K makes the MFC aerogels a promising insulating material over other commercial heat-insulating products and cellulose aerogels. By owning excellent characteristics, the MFC aerogels could be utilized in various fields such as sound insulation, oil adsorption, and flame retardant materials.

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