Enhanced flame resistance of cellulose aerogel by ammonium polyphosphate for heat insulation

Nguyen Tan Luon[1,2], Phan Le Bao[1,2], Do Nguyen Hoang Nga[1,2], Mai Thanh Phong[1,2],
Le Van Thang[2,3], Le Anh Kien[4], Le Thi Kim Phung[1,2,*]

[1]Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Vietnam;
[2]Vietnam National University Ho Chi Minh City, Linh Trung Ward, Thu Duc District, Ho Chi Minh City, Vietnam;
[3]Faculty of Materials Technology, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Vietnam;
[4]Institute for Tropical Technology and Environmental Protection, 57A Truong Quoc Dung Street, Phu Nhuan District, Ho Chi Minh City, Vietnam.
*Corresponding author: phungle@hcmut.edu.vn

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ABSTRACT

Cellulose aerogels are a potential candidate for heat insulation, but one of their drawbacks is high flammability hindering their applications in practice. This study synthesized cellulose aerogels from microfibrillated cellulose fibers (MFC) extracted from discarded pineapple leaves. The procedure started with simply mixing the extracted fibers with polyamide amine-epichlorohydrin (PAE) as a chemical crosslinker and ammonium polyphosphate (APP) (10-20%) as a green and effectively flame-resistant additive, followed by freeze-drying. The produced aerogels are characterized in terms of their morphology, thermal stability and conductivity, and flame resistance via advanced and standardized methodologies including Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), thermal conductivity measurement by a heat flow meter, and UL94 horizontal burning test. The flame-resistant cellulose aerogels exhibit ultra-low density (25.5-26.8 mg/cm^3), high porosity (98.0-98.2%), excellent heat insulation (35.9-36.7 mW/m·K), and are completely flame-resistant. In addition, the varied APP content (10-20%) shows little effect on the density, heat conductivity, and thermal stability of the flame-resistant cellulose aerogels in comparison with that of the neat cellulose aerogel. Based on the findings, the synthesized flame-resistant cellulose aerogels are considered a promising bio-based heat insulation material.

Keywords: Microfibrillated cellulose; Pineapple leaves; Aerogel; Thermal insulation; Flame resistance.

1. INTRODUCTION

Among the most promising porous materials of the 21st century, aerogels recently have many potential applications in various fields. They have an extremely low density (1.1–500.0 mg/cm^3), high porosity (up to 99.8%), huge specific surface area (10–2000 m^2/g) [1], low thermal conductivity (e.g. as low as 13 mW/m·K for silica aerogel) [2], and high noise reduction coefficient (NRC) (e.g. cellulose aerogels can achieve NRC of 0.52) [3]. Moreover, their surface can be modified by chemical reactions to produce a wide range of surface-active properties. Based on their outstanding properties, aerogels are widely applied for adsorption, energy storage, heat insulation, sound absorption, etc. Nowadays, many materials, such as polymers, carbonaceous materials, metal/metal oxides, silica-based materials, etc., have been used for fabricating aerogels [1]. Noticeably, biomass/biopolymer aerogels have recently been gaining more and more popularity due to their natural abundance, cost-efficiency, eco-friendliness, and biodegradability. The major raw materials for the synthesis of biomass-based aerogels are agricultural waste (e.g., sugarcane bagasse, coconut coir, pineapple leaves, rice straw, etc.) or byproducts from the food processing sector (e.g., crab, prawns, and shrimp shells, etc.). Those residues can cause many environmental problems via burning, landfilling, or discharging directly into the environment, which releases many pollutants. In Vietnam's agricultural sector, pineapple is one of the largest fruit harvests, with a total cultivated area in 2019 of 39,158 ha [4]. Accompanied by substantial pineapple production, the amount of waste from pineapple trees in Vietnam, including leaves, peels, seeds, and unused flesh, is also considerable, over 1 million tons annually [5]. However, the fibers produced from pineapple leaves are valuable due to their high proportion of cellulose (approx. 36%) and high mechanical strength (compression module from 34.5 to 82.5 GN/m^2, tensile strength from 413 to 1627 GN/m^2) [6, 7]. Therefore, pineapple fibers are favorable for fabricating cellulose-based ultra-light aerogel. In 2020, Do et al. synthesized aerogels from pineapple fibers which exhibit ultra-low density (13–33 mg/cm^3), high porosity (above 96%), great Young's modulus (1.64–5.73 kPa), low thermal conductivity (30–40 mW/m·K), and high NRC (approx 0.52) [3].

Nowadays, the demand for transport, refrigeration systems, domestic appliances, modern energy-efficient building construction, etc., requires thermal insulation materials. Because of their low density (below 350 mg/cm^3), high porosity (84.0-99.9%), low thermal conductivity (23.0-75.0 mW/m·K), and their advantages related to environment and economy, cellulose aerogels are potential candidates for those applications [8]. The thermal conductivity of cellulose aerogels is strongly associated with their density and porosity. As the density decreases and the porosity rises, this will lead to a downturn in the heat conductivity of cellulose aerogels [9]. Compared with cellulose-based aerogels, microfibrillated cellulose (MFC) aerogels express a lower density (29.1–36.1 mg/cm^3) and higher porosity (97.4–98.0%) [10]. This is the sound foundation for a lot of recent research focusing on developing thermal insulation materials from MFC. However, the limiting oxygen index (LOI) of pure cellulose is only 19% which means they are highly inflammable [11]. That is one of the major drawbacks of aerogels fabricated from MFC. This problem could be addressed by either adding flame-retardant additives (e.g., sodium bicarbonate ($NaHCO_3$), ammonium polyphosphate (APP), etc.) or in-situ formation of flame-retardant agents (e.g., silica (SiO_2), magnesium hydroxide ($Mg(OH)_2$), etc.) with the expectation of minimal effect on insulation properties as well as thermal and mechanical stability of aerogels [9, 11, 12]. In 2017, Li and Wang combined the polymerization of dopamine and hydrolysis of organosilicon in cellulose nanofiber (CNF) suspension, followed by freeze-drying. The obtained aerogels expressed a self-extinguishing property, low density (15.1–28.5 mg/cm^3), and desirable compression strength (76.6–135.8 kPa) but high thermal conductivity values (~46 mW/m·K) [12]. Muhammad Farooq et al. (2017) fabricated CNF aerogels by integrating sodium bicarbonate (SBC) as the fire retardant without affecting the thermal conductivity of the aerogels (approx. 28 mW/m·K). The minimum burning velocity of those resulting aerogels was 0.20 cm/s at 40 wt% of SBC in comparison with 5.84 cm/s of pure CNF aerogels [12]. This method is low-cost, industrially efficient, and environmentally friendly, but the obtained aerogels still get burned despite the high proportion of SBC. Among the flame-retardant additives, ammonium polyphosphate (APP) captures a great deal of attention because of its high flame-retardant character, eco-friendliness, no hazardous effects on humans, and cost-effectiveness [8]. In 2019, Huang et al. improved the flame-retardant property of polyvinyl alcohol (PVA)/CNF aerogel by microencapsulated APP (5.3-13.3 wt% of dry CNF). Although the material became self-extinguished, their density and thermal conductivity rose significantly to 60.0 mg/cm^3 and 41.2 mW/m·K, respectively, compared to the non-microencapsulated APP aerogel, at 47.0 mg/cm^3 and 38 mW/m·K in that other [13]. In 2021, MinYi Luo et al. used APP to enhance the anti-combustion character of PVA-based aerogels, which are crosslinked by chitosan (CS) and boric acid (H_3BO_3). The time to ignition (TTI) of the PVA-based aerogels was up to 156 s compared to 66 s of those having APP (15.6-46.9% of PVA). The aerogels exhibited high thermal conductivity (approx 87.9 mW/m·K) as well as many chemicals were included in the synthesis process [14].

Therefore, in this study, heat-insulating cellulose aerogel has been fabricated for the first time from abundant pineapple leaves and polyamide amine-epichlorohydrin (PAE), a common green crosslinking agent mainly used in the papermaking industry via a simple procedure. APP with different contents (10-20 wt%) was added to cellulose aerogel to create a flame-resistant aerogel with marginal change in its thermal conductivity. The density, porosity, morphology, thermal conductivity and stability, and burning velocity of the obtained aerogels were examined by advanced and standardized methods.

2. EXPERIMENTAL

2.1. Materials

Pineapple leaf (PL) fibers were supplied from Nghe An province, Vietnam. Sodium hydroxide (NaOH, purity 96%), ammonium polyphosphate (APP), hydrogen peroxide (H_2O_2, 40 wt%), and sulfuric acid (H_2SO_4, 98 wt%) were purchased from Xilong Scientific Co., Ltd., China. Polyamide amine-epichlorohydrin (PAE) was obtained from Shandong Bluesun Chemical Co., Ltd., China. All solutions were prepared in reverse osmosis (RO) water.

2.2. Preparation of microfibrillated cellulose (MFC)

Raw pineapple leaves were grounded to fine powders (50 mesh size) and then treated with a 3 wt% NaOH solution with a liquid-to-solid mass ratio of 20:1 for 2 h, at 80 °C. The alkaline treatment was repeated three times. The pulps were then rinsed with RO water until neutral pH. After that, the dry obtained solid was bleached with a mixture of 10 wt% H_2O_2 and 1 wt% NaOH solution (ratio of 1:1 in volume) at a liquid-to-solid mass ratio of 20:1 for 1 h, at 80 °C. Finally, the cellulose-rich pulp, denoted as BPL, was recovered after filtration, rinsing with RO water until pH-balanced, and drying in an oven at 80 °C overnight. The solid recovery for BPL from raw pineapple leaves reached approximately 44.6%.

BPL was hydrolyzed in a 40 wt% H_2SO_4 solution at a liquid-to-solid mass ratio of 20:1 for 3 h, at 45 °C. This step was terminated by adding RO water, and the obtained mixture was settled down over time. The upper layer of water separated from the suspension was removed periodically, introduced fresh water until the suspension reached neutral pH. Finally, the obtained mixture was homogenized for 2 h at 15000 rpm to achieve microfibrillated cellulose named MFC. H_2SO_4 and NaOH from wastewater could be recovered by distillation and crystallization for reusing.

2.3. Preparation of flame-resistant cellulose aerogel

Firstly, suspensions of MFC (1 wt%) and BPL (1 wt%) were mixed with a weight ratio of 3:1 to achieve a cellulose suspension (1 wt%). After that, PAE (80 wt% of dry cellulose) and APP (10-20 wt% of dry cellulose) were introduced to the re-prepared cellulose suspension and vigorously stirred for 15 min. The obtained mixture was then refrigerated for 24 h before lyophilizing using a Toption TPV-50F lyophilizer under the vacuum condition for 48 h. The final flame-retardant cellulose aerogel was achieved after heat annealing in an oven for 3 h, at 120 °C.

2.4. Characterization

The bulk density of each aerogel sample is calculated as a ratio of its weight and volume. The porosity (φ (%)) is determined using the bulk density ($\boldsymbol{\rho_a}$ (mg/cm^3)) and the average skeletal density of components ($\boldsymbol{\rho_b}$ (mg/cm^3)) as shown in Eq.1:

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

The average skeletal density ($\boldsymbol{\rho_b}$ (mg/cm^3)) of the composite was determined using Eq.2:

$$\rho_b = \frac{1}{\sum \frac{W_i}{\rho_i}} \tag{2}$$

Where $\boldsymbol{W_i}$ and $\boldsymbol{\rho_i}$ are respectively mass fraction and skeletal density of each component in the material. The skeletal density of MFC, BPL, PAE and APP are assumed as 1.46, 1.35, 1.15, and 1.90 g/cm^3, correspondingly [5].

Field Emission-Scanning Electron Microscope (FE-SEM, Hitachi S4800) was used to investigate the morphology of the aerogel samples. Each sample was coated with a thin layer of Pt before testing, and the test was conducted at an acceleration voltage of 10 kV. A TGA analyzer (LINSEIS DSC PT 1600) was applied to evaluate the thermal stability of the aerogels. The samples were heated from 30 °C to 700 °C at a heating rate of 5 °C/min in the air flow rate of 20 mL/min. The thermal conductivity of the aerogels was examined at room temperature by using the HFM-100 Heat Flow Meter (Thermtest Inc., Canada). The procedure adapted from the UL-94 horizontal test was applied to examine the flammability of the samples. The standard tested samples were around 1.3 cm wide, 6 cm long, and 1 cm thick. They were ignited for 3 s before freely flaming. A digital camera was used to record the whole combustion process, and the combustion velocity (V (mm/s)) was determined by the following equation:

$$V = \frac{L}{t} \tag{3}$$

In Eq.3, L (mm) is the burned length, and t (s) is the time of burning.

3. RESULTS AND DISCUSSION

3.1. Density and porosity of cellulose aerogels

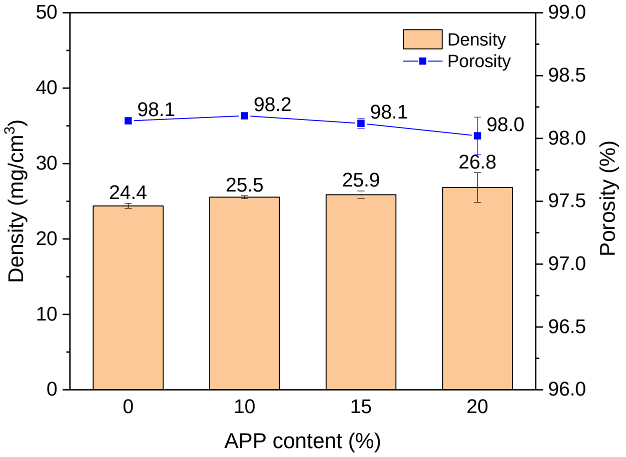

***Figure 1.** Density and porosity of cellulose aerogel as a function of APP content.*

Figure 1 illustrates the density and porosity of the cellulose aerogel samples containing different APP contents. In terms of density, the neat cellulose aerogel is slightly lighter than the cellulose aerogels with APP. As the APP content increases from 10 to 20%, the aerogel density climbs minimally by 1.3 mg/cm^3. This is attributed to the growth in the solid concentration after adding the flame retardant agent. As a result, the porosity of the cellulose aerogel reduces gradually from 98.2 to 98.0%, corresponding to the APP content rising from 10 to 20%. In general, their density and porosity are much lower than other flame-retardant aerogels, such as

PVA/APP aerogel (482-763 mg/cm^3, 73.2-87.1%) and PVA/CNF/ microencapsulated APP aerogel (50-60 mg/cm^3) [11, 13].

3.2. Morphology of cellulose aerogels

The SEM images (figure 2) reveal that all samples have a 3D porous structure, with BPL playing the role of the main framework, which fosters the mechanical strength of the aerogels. MFC with 2-3 μm in diameter and 20-40 μm in length distributes into empty spaces between BPL, and thus the presence of MFC leads to the reduction of the pore size [9]. After the introduction of the flame retardant additive, new thin films appear on the surface of the material. This film formation will then prevent the materials from further burning [14].

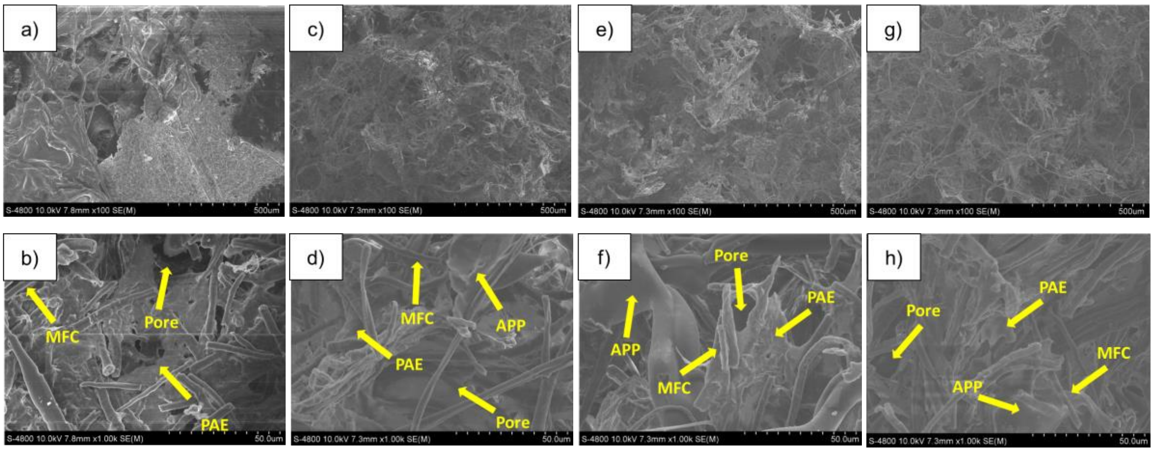

Figure 2. *Morphology of neat cellulose aerogel (a,b), cellulose aerogels with 10% (c,d), 15% (e,f), 20% (g,h) of APP.*

3.3. Flame retardancy of cellulose aerogels

The result of the burning test is presented in figure 3. Initially, the pure cellulose aerogel is quickly burned in the air with an average burning rate of 5.3 mm/s. Noticeably, after collaborating with APP, the aerogel could self-extinguish after three seconds of initial burning. During the burning test, there is a formation of char layers on the outer surface of the material. These char layers play a role in preventing the indoor substrate from contacting oxygen and transferring heat subsequently [14]. This points out that APP is an excellent flame retardant additive for the material. In addition, there is almost no difference in the burning characteristics of the aerogel with the APP proportion in the range of 10-20%, suggesting that high flame repellency could be obtained even at a very low APP content (10%).

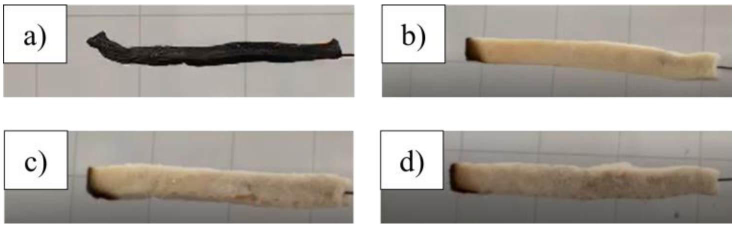

Figure 3. *Photographs of cellulose aerogel (a) and cellulose aerogels with 10% (b), 15% (c), 20% (d) of APP after horizontal combustion test.*

3.4. Thermal conductivity of cellulose aerogels

Figure 4 gives information about the heat conductivity of the neat cellulose aerogel and flame-repellent cellulose aerogels. The thermal conductivity of the neat cellulose aerogel is around 36.1 mW/m·K. Remarkably, there is almost no change in the thermal conductivity of the material after introducing APP (35.9-36.7 mW/m·K). On the one hand, the APP contents are too small that have little effect on the thermal conductivity of the solid phase. In addition, introducing APP does not make significant changes in the density and porosity (figure 1), which mainly contribute to the heat conductivity of the gas phase. Therefore, almost no change was seen in the overall heat conductivity following the increase in APP content. In general, the obtained thermal conductivity is comparable to aerogel from pineapple leaf and cotton waste fibers (39.0-43.0 mW/m·K) [7], PVA/CNF/microencapsulated APP aerogel (39.0-41.3 mW/m·K) [13], and other commercial insulation materials such as extruded polystyrene (29.0-48.0 W/m·K) and foam glass (38.0-50.0 W/m·K) [15].

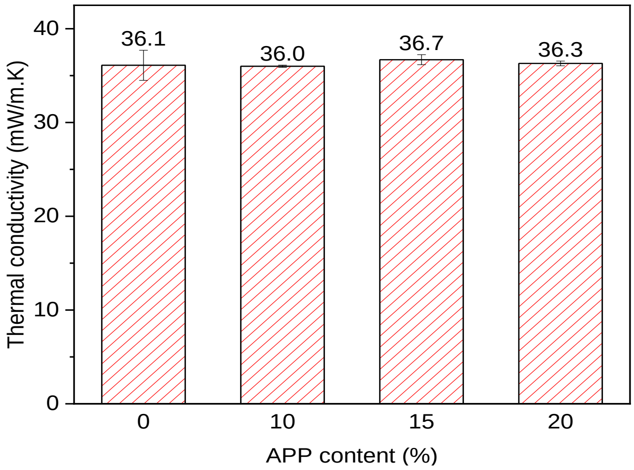

Figure 4. *Effect of APP proportion on thermal conductivity of cellulose aerogel.*

3.5. Thermal stability of cellulose aerogels

The effect of APP on the thermal stability of the cellulose aerogels could be seen in TGA and DTA curves, as presented in figure 5. There is a small reduction of 8-10% in the materials' mass at below 100 °C due to moisture evaporation. This endothermic process could be observed in the DTA curve with a downward peak of around 80 °C. The major mass-reducing step starts from around 220 °C attributed to the decomposition of cellulose and PAE, with the two exothermic peaks at nearly 310 °C and 480 °C. Noticeably, at 550 °C, the char residue increases significantly from 0.6% to above 22% after introducing APP. In addition, this figure climbs from 22.7 to 27.5% as rising APP content from 10 to 20%. Therefore, the presence of APP acts as a catalyst for the dehydration of cellulose to form char, the main cause of flame-retardance [11].

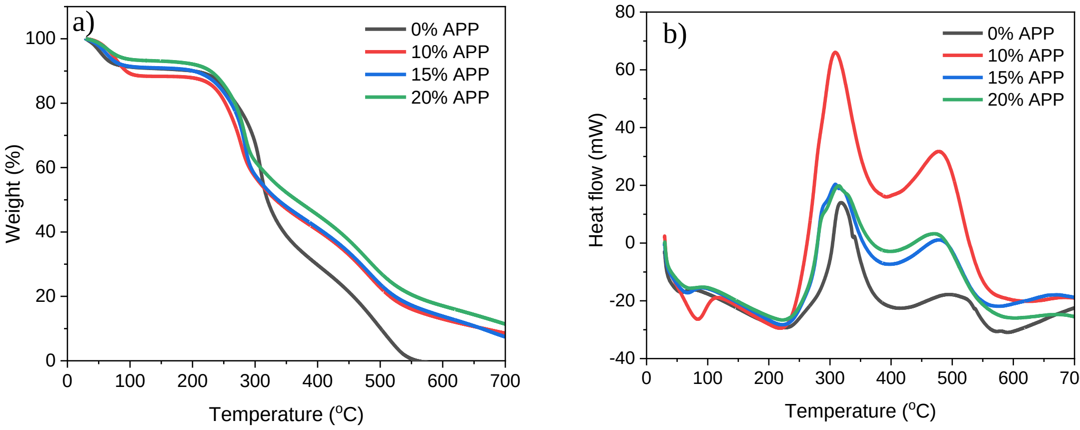

Figure 5. *TGA (a) and DTA (b) curves of cellulose aerogels with various APP contents.*

4. CONCLUSIONS

The flame-resistant cellulose aerogel from discarded pineapple leaves was successfully fabricated by a facile and cost-effective method with safe and non-toxic ingredients. The obtained aerogels are lightweight (25.5-26.8 mg/cm^3), highly porous (98.0-98.2%), and thermally insulating (35.9-36.7 mW/m·K). The cellulose aerogel with different APP proportions (10-20%) has the same self-extinguishing characteristic and almost no differences in terms of density, porosity, and heat conductivity in comparison with the neat cellulose aerogel. Overall, the fabricated aerogel is a good candidate for thermal insulation application. The preparation of the flame-resistant cellulose aerogel should be comprehensively studied and optimized for large-scale production.

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TÓM TẮT

Tăng cường tính chống cháy của cellulose aerogel bằng ammonium polyphosphate cho ứng dụng cách nhiệt

Cellulose aerogel là một ứng cử viên tiềm năng cho vật liệu cách nhiệt, thế nhưng một trong những nhược điểm của chúng chính là tính dễ cháy cản trở việc ứng dụng chúng vào thực tế. Nghiên cứu này tổng hợp cellulose aerogel từ vi sợi cellulose (MFC) trích xuất từ lá dứa thải. Quy trình tổng hợp vật liệu bắt đầu bằng cách phối trộn trực tiếp sợi MFC với polyamide amine-epichlorohydrin (PAE), một chất liên kết ngang hóa học và ammonium polyphosphate (APP) (10-20%), một chất phụ gia chống cháy an toàn và hiệu quả, sau đó hỗn hợp được sấy thăng hoa. Các aerogel sau khi tổng hợp được đánh giá các đặc trưng của chúng như hình thái học, độ bền nhiệt, hệ số dẫn nhiệt, khả năng chống cháy bằng các phương pháp phân tích hiện đại bao gồm kính hiển vi điện tử quét (SEM), phân tích nhiệt trọng lượng (TGA), đo độ dẫn nhiệt bằng thiết bị chuyên dụng đo lưu lượng nhiệt, và thử nghiệm đốt theo phương ngang UL94. Vật liệu cellulose aerogel cho thấy khối lượng riêng cực kì thấp (25,5-26,8 mg/cm^3), độ xốp cao (98,0-98,2%), khả năng cách nhiệt hiệu quả (35,9-36,7 mW/m·K), và hoàn toàn có khả năng tự dập tắt sự cháy. Hơn nữa, hàm lượng APP (10-20%) không ảnh hưởng đáng kể đến khối lượng riêng, hệ số dẫn nhiệt, và độ bền nhiệt của cellulose aerogel chống cháy khi so sánh với cellulose aerogel không chứa chất chống cháy. Dựa trên các kết quả thu được, vật liệu tổng hợp cellulose aerogel chống cháy có thể xem là một vật liệu cách nhiệt có nguồn gốc sinh học đầy hứa hẹn.

Từ khoá: Vi sợi cellulose; Lá dứa; aerogel; Vật liệu cách nhiệt; Chậm cháy.