Chemical Engineering Journal 327 (2017) 992–999

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Rejuvenated fly ash in poly(vinyl alcohol)-based composite aerogels with high fire safety and smoke suppression

A-Hui Kang [a], Ke Shang [a], Dan-Dan Ye [a], Yu-Tao Wang [a], Han Wang [a], Zong-Min Zhu [a], Wang Liao [a,*], Shi-Mei Xu [a], Yu-Zhong Wang [a,*], David A. Schiraldi [b]

[a] Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610064, China
[b] Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202, United States

HIGHLIGHTS

- A waste of fly ash is used for flame retardant lightweight aerogel.
- The ratio of the utilized waste fly ash is as high as 76.5 wt%.
- Oxides in the fly ash particles remarkably suppress heat release and smoke release in fire.

ARTICLE INFO

Article history:
Received 17 April 2017
Received in revised form 3 June 2017
Accepted 27 June 2017
Available online 29 June 2017

Keywords:
Aerogel
Fly ash
Polyvinyl alcohol
Fire safety
Smoke suppression

ABSTRACT

As a by-product of thermal power plants, a large amount of fly ash (FA) was produced every year. The comprehensive utilization of fly ash has been receiving increasing attention around the world. In this paper, FA simply modified with NaOH was used to enhance the flame retardancy of poly(vinyl alcohol) (PVA)/Laponite (Lap) aerogels via an environmentally friendly freeze-drying method. From the cone calorimetry test, it was obvious that the heat release rate, total heat release, smoke produce rate and total smoke production of the composite aerogels were decreased significantly with the addition of FA. When the content of fly ash exceeded 63.6 wt%, the limiting oxygen index exceeded 60.0%. All the PVA/Lap/FA aerogels reached V-0 ratings in vertical burning test. The thermal stabilities of the PVA/Lap/FA aerogels improved compared with PVA/Lap aerogels by thermogravimetric analysis. The addition of FA can effectively reduce the calorific value of aerogels, and achieved 2.50 MJ/kg when the FA content reached 76.5 wt%. After disposed with ultrasonic cell crusher, the PVA/Lap/FA mixtures became more homogeneous and form the more regular microstructures after freeze-drying, meanwhile, the pore size became smaller with the increase of FA. The PVA/Lap/FA aerogels exhibited stronger mechanical properties, which compression modulus and strength enhanced a lot than PVA/Lap aerogels. The introduction of FA into PVA/Lap aerogels improved their flame retardant properties successfully, demonstrating it a fire safety product. The content of FA has been achieved more than 50 wt% which provided a new method for efficient utilization of FA.

1. Introduction

Coal is among the most vital power sources on earth. In the Top 3 countries using coal to generate power, it takes up 50.2% in China, 10.6% in India and 10.3% in the United States in 2015 [1]. After combustion, the residue of coal is fly ash (FA), which certainly has an astonishing huge production. For instance, generation of FA in China was around 550 million tons in 2012 [2]. Well-developed usages of FA include light-weight additive for cement, concrete and pavement [3]. Newly developed applications of FA are various as adsorbents for flue gas (SO_x [4], NO_x [5] and gaseous organics [6]), removal of chemical pollutants (toxic metals [7–10], organic compounds [11–13] and other inorganic components [14,15]) from wastewater, preparation of zeolite [16–18], mesoporous silica [19] and combination into silica aerogels [20–22], etc. However, the scale of FA usage is far from enough. The comprehensive utilization ratio of FA was only ca. 69%. [2] How to use the massive rest has been attracting worldwide attention, for it's just disposed in open

---

* Corresponding authors.
E-mail addresses: liaowang@scu.edu.cn (W. Liao), yzwang@scu.edu.cn (Y.-Z. Wang).

http://dx.doi.org/10.1016/j.cej.2017.06.158
1385-8947/

landfills and lagoons and therefore results in severe environmental problems, such as air pollution and river clogging [3].

On the other hand, the usage of the power generated is wasteful. Especially in the building area, more than tenth of the total energy is used for indoor environment [23]. In China, for instance, building energy consumption amounted to 27.5% in 2012 [24]. Moreover, the total building area is expected to continuously increase to 70 billion m^2 by 2020 [25], indicating a huge demand for external wall insulation material. In this area, organic foams, such as expanded polystyrene foam (EPSF) and rigid polyurethane foam (RPUF), are the first choices currently. But as they are well-known for the fire risky and difficulty in combination of flame retardancy in an eco-friendly way [26,27]. Aerogels are taken as novel foam-like materials with low densities, high surface areas and thermal conductivities [28–33], and therefore promising candidates for building isolation. Among them, organic-inorganic composite aerogels [32,34–38] overcome the brittleness of inorganic aerogels and relieve the cost consideration of carbon aerogels.

Polyvinyl alcohol (PVA) and nanofillers, such as montmorillonite (MMT), Laponite (Lap), halloysite and SiO_2 composite aerogels have been prepared and the heat release, smoke release of the aerogel composites significantly decreased with these nanofillers [39]. However, the limiting oxygen index (LOI) values only improved from 22% to 25%, and not passed the V-0 ratings in UL-94 test. Wang et al. used piperazine-modified ammonium polyphosphate to improve the flame retardancy of PVA/MMT aerogels and maintained their mechanical properties [31]. The smoke production of this composite aerogels, however, increased significantly during the combustion. In addition, materials with organic polymer are very difficult to meet high fire safety requirements.

The chemical composition of FA vary with the types of the coal and combustion conditions. Even so, the basic components of FA are SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O and unburned carbon [3,40]. These inorganic oxides in FA have been recognized as an inert fillers that dilute the content of combustible in the samples. The transition metal (Fe_2O_3) can promote the crosslinking of polymer to form dense char layer [41]. Al_2O_3, SiO_2, MgO, Fe_2O_3 act as good co-synergist with red phosphorus or intumescent flame retardant to improve the fire properties of polymer materials (polypropylene, poly (ethylene terephthalate), PET, etc.) [42–44]. Soyama et al. investigated that the flame retardancy of polycarbonate resin was improved by addition of FA [45]. The hydrogen bond between the hydroxyl group of FA and polycarbonate resin primarily improved the heat resistance of polycarbonate resin and isomerized the polycarbonate to promote carbonization. The LOI of urea-formaldehyde-based particleboard from hazelnut shells was increased from 22.3% to 38.2% with FA [46]. Qin et al. prepared FA-stabilized Pickering foams which can effectively retard the oxidation of coal and reduce the risk of coal spontaneous combustion [47]. However, the ratio of FA in these materials are always no more than 50% for the compromise of mechanical strength of the resultant materials.

In this work, we demonstrate a concept composite aerogel using water soluble polymer of PVA and a nanoclay of Lap to agglutinate the FA to form an aerogel. The high solubility in water, relatively low cost and multi hydrogen bonding points make PVA an outstanding candidate for the polymer portion in composite aerogels. Lap is a synthetic nanoclay with a permanent negatively charged surfaces and positively charged edges when dispersed in water [35]. A small amount (>ca. 2 wt%) of this clay tends to form a hydrogel with a morphology of 'house of cards' [36]. Preparation of the aerogel combines the easy gelling capability of Lap and Lap-PVA, and totally under an aqueous condition. These aerogels are with high fire safety, smoke suppression, low thermal conductivity and usable mechanical strength. More importantly, utilization of FA can reach as high as 76.5 wt% in the final product. These characteristics make the aerogels promising building isolation materials. The reciprocal interactions, which are responsible for above mentioned advantages, between the ingredients are investigated.

2. Experimental section

2.1. Materials

Poly(vinyl alcohol) (PVA) 1799 and sodium hydroxide (NaOH, Analytical reagent) were purchased from kelong Chemical Company (China). Laponite XLG (Cation exchange capacity (CEC) = 50–55 mequiv/100 g) was obtained from BYK Additives & Instruments. Fly ash (FA) was received from National Institute of Clean-and-Low-Carbon Energy. The components and characteristics of the FA were determined and presented in Table 2 and Fig. 1.

2.2. Preparation of aerogels

FA (100 g) was soaked in 10 M NaOH solution (200 ml) following a procedure similar to that reported by Chris White [48]. The preparation process of PVA/Lap/FA aerogels was briefly shown in Scheme 1. To produce an aerogel composite containing PVA, Lap and FA, for example, 2 g PVA was dissolved in 20 mL of DI water at 90 °C to create 10 wt% PVA solutions. 2 g Lap was dissolved in 60 ml of DI water with magnetic stirring. 4 g FA was dispersed in 20 ml of DI water. The Lap and FA dispersion were mixed, and then PVA solution was added into this dispersion under magnetic stirring.

The mixture was put into the ultrasonic cell crusher (40% power) for 10 min to well dispersed and remove the bubbles. The resulting mixture was poured into polytetrafluoroethylene (PTFE) mold and immediately frozen in liquid nitrogen. The frozen samples were then freeze-dried using a lyophilizer (LGJ-50 F, Ningbo Xinyi ultrasonic equipment Co. Ltd. China) from −20 °C to 25 °C and 0.1 Pa. After 3–5 days the samples were moved from the freeze-dryer to a vacuum oven with further drying at 60 °C for 6–24 h to produce the final product. The resultant sample is named $P_2L_2F_4$, in which P refers to PVA, L refers to Lap and F refers to FA, and the corresponding subscript indicates its weight percentage in water. The recipe for all samples is shown in the Table 1.

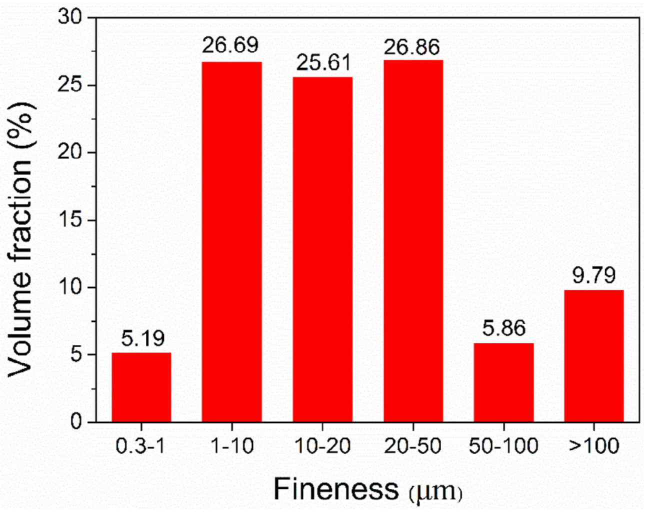

Fig. 1. Fineness distribution of FA particles in this work.