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Communication

Thermally stable and flame-retardant poly(vinyl alcohol)/montmorillonite aerogel *via* a facile heat treatment

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ABSTRACT

Poly(vinyl alcohol)/montmorillonite aerogels with high thermal stability and flame retardancy were prepared with a facile heat treatment method, in which the poly(vinyl alcohol)/montmorillonite aerogels was first prepared by an eco-friendly freeze-drying method, following by a heat treatment process. The structure of the aerogels before and after heat treatment process was characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The thermal stability of the aerogel treated for 3 h at 200 °C was improved significantly, which was accompanied by a slight decrease of mechanical property. Meanwhile, cone calorimetry (CC) test revealed that the flame-retardant performance of the heat treated aerogel was improved remarkably.

Inorganic silica-based aerogels are the earliest and widely-used aerogels, which possess super low densities and are generally nonflammable, but the poor mechanical property and high production cost remarkably limit their applications [1,2]. In contrast, polymer/clay composite aerogels [3–5], which combine the advantages of the polymer and the clay and easily overcome the fragility of the silica aerogels, have aroused heterogeneous interests because of their high performances. Moreover, these composite aerogels are always prepared by freeze-drying method with water as the solvent, making the preparation process facile, environmentally friendly and cost economic. Consequently, polymer/clay composite aerogels are highly promising for various areas, such as oil contaminant removal [6,7], drug delivery [8], building insulation [9], *etc.*

Polyvinyl alcohol (PVA) is a proper candidate for polymer/clay composite aerogels for its highly hydrophilic, nontoxic and mechanically strong. Chen *et al.* [10] prepared PVA-based composite aerogels with several clays and nano silica, and studied the performances of the aerogels. Clays can migrate to the surface which is driven by the lower surface free energy compared with carbon-based polymers and promote the formation of a protection layer [11,12]. The flame retardant property of the sample is thus improved. However, the protective barrier formed by MMT in the fire region mainly retards the flame spread rather than reduce fire load, ignitability or flammability of the material [13]. Because PVA is a highly flammable polymer, the PVA-based composite aerogels are still with fire risky. Higher fire resistance could be achieved by addition of effective flame retardants, such as ammonium polyphosphate (APP) [14], but they had poor compatibility and dispersion with the polymer. Wang *et al.* [15] used piperazine-modified APP (PA-APP) instead of APP to maintain the mechanical strength of the aerogels. However, a negative impact on the strength is inevitable.

Herein, we demonstrate a facile heat treatment method to improve the thermal stability and flame retardancy of the PVA/MMT composite aerogel. After a high temperature treatment, PVA decomposed with partial elimination of hydroxy groups. Consequently, the thermal stability and flame retardant performances of the aerogels were improved significantly.

Poly(vinyl alcohol) (PVA) having a polymerization degree of 1000 or more and a saponification degree of 99 mol% or more (PVA-1799) were supplied by Kelong Chemical Reagent Corporation (Chengdu, China). Sodium montmorillonite (Na^+-MMT; PGW grade; cation exchange capacity (CEC) 145 meq/100 g) was purchased from Nanocor Inc. All ingredients were used without further purification.

A 5 wt% aqueous solution of PVA was prepared by dissolving 5 g PVA to 100 mL DI water at 90 °C under stirring for 8 h. 5 g MMT was

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mixed with 100 mL of 5 wt% PVA solution at 14.000 rpm (A-555, INAYOU, China) to prepare a PVA/MMT solution. The PVA/MMT solution was then poured into a mold and frozen with liquid nitrogen, following with freeze drying using a VFD-1000 lyophilizer (Boyikang Co., Ltd., China) at −20 °C with an air pressure < 1 Pa. The resultant aerogel was named P5M5, where P and M denotes to PVA and MMT, respectively, and the numbers refer to the percentages of these materials in water. The freeze-dried aerogels were then treated in a vacuum oven at 150 °C or 200 °C for 3 h to prepare the final aerogels, which were named P5M5-150 and P5M5-200, respectively.

Fourier transform infrared (FTIR) spectroscopy was used to characterize the structural changes of the aerogels through a heat treatment process. The FTIR spectra were shown in Fig. 1. The peak at about 3300–3400 cm^{-1} represents the stretching vibration of hydroxyl. The peak intensity decreases with the treatment of 150 °C and increases with the treatment of 200 °C. A new peak can be observed in the FTIR spectra of P5M5-200 at 1713 cm^{-1}, which belongs to C=O. By comparison [16,17], we can speculate that the hydroxyls of the sample dehydrated into ether bonds at 150 °C and the ether bonds fractured at 200 °C subsequently. Finally, partial elimination of hydroxyl groups was achieved with subsequent formation of carbonyl groups.

To further confirm the conjecture, X-ray photoelectron spectroscopy (XPS) was conducted. Fig. 2 shows the C_{1s} and O_{1s} spectra of P5M5, P5M5-150 and P5M5-200. For P5M5-200, a new peak can be observed at the binding energy of 287.0 and 531.2 eV in the C_{1s} and O_{1s} spectra, respectively, which belong to chemical bond of C=O and correspond to the previous results. However, because the binding energy of C—O—C is close to that of C—O (the binding energy of 286.3 eV in C_{1s} spectra and 532.9 eV in O_{1s} spectra), it is difficult to discuss the XPS results of the aerogel treated at 150 °C.

The density and mechanical property of P5M5 and the heat treated aerogels are summarized in Table 1. The density of P5M5-150 was closed to the control. As PVA was decomposed in advance, the mass of the sample decreased while the volume did not vary, resulting in a density reduction for P5M5-200. The heat treatment process decreased the mechanical strength of the aerogels, for the hydrogen bonding interaction between PVA and MMT was partially destroyed. As compensation, the formation of covalent crosslinking bond (C—O—C) in P5M5-150 sample replaced part of the loss of mechanical property, therefore, the compressive modulus of P5M5-150 was relatively higher than that of P5M5-200.

Fig. 3 shows TGA weight loss and corresponding DTG curves of P5M5, P5M5-150 and P5M5-200 aerogels, the deduced key parameters, including the onset decomposition temperature (defined as the temperature at which 5 wt% weight loss takes place, or $T_{d5\%}$), the maximum decomposition temperature (T_{dmax}), the decomposition rate at the T_{dmax} (dW/dT) and the residual weight (%) are summarized in Table 2. Because MMT only released a little crystalline water, as a result, the decomposition of PVA/MMT composite aerogel was mainly the decomposition of PVA chains, which was indicated by two peaks at 280–290 °C for the removal of hydroxyl groups and at 410 °C for decomposition of the main chain, respectively. The hydrophilic property of MMT made a little peak appear before 100 °C, leading to a lower T_{dmax} of P5M5 aerogel compared with neat PVA aerogel. The results showed that the thermal stability of P5M5-150 had little change compared with that of the control. After heat treatment at 200 °C, the thermal stability of the aerogel improved significantly due to the decomposition of hydroxyl groups in advance. $T_{d5\%}$ and T_{dmax} of P5M5-200 increased by 53.4 °C and 63.6 °C comparing with those values of P5M5, respectively. The polymer content decreased for P5M5-200 because elimination of hydroxy groups resulted in an increase of residual weight. The obvious decrease of the decomposition rate at the T_{dmax} and increase of residual weight also demonstrated a remarkable improvement of thermal stability for the aerogel.

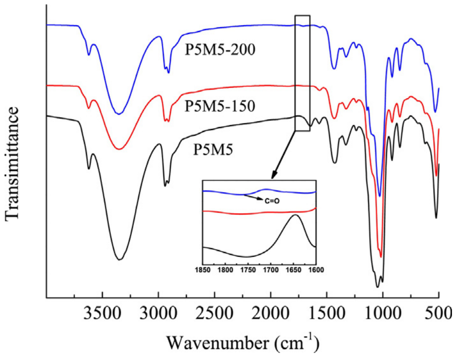

Fig. 1. FTIR spectra of the heat treatment aerogels.

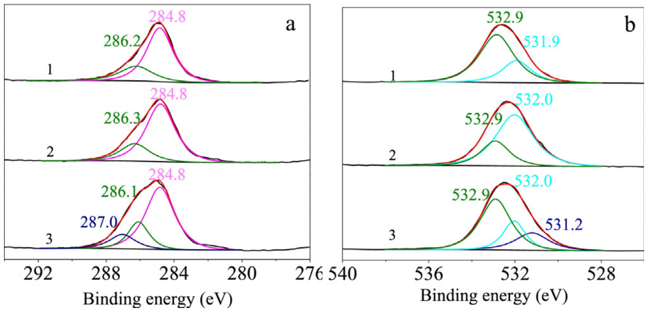

Fig. 2. Spectra of X-ray photoelectron spectroscopy for P5M5 (1), P5M5-150 (2) and P5M5-200 (3) in a muffle for 3 min in N_2 atmosphere: C_{1s} (a) and O_{1s} (b).

Table 1
Density and mechanical property of P5M5, P5M5-150 and P5M5-200 aerogels.

Sample	Density (g/cm^3)	Modulus (MPa)
P5M5	0.0918	20.5
P5M5-150	0.0932	17.9
P5M5-200	0.0801	15.5

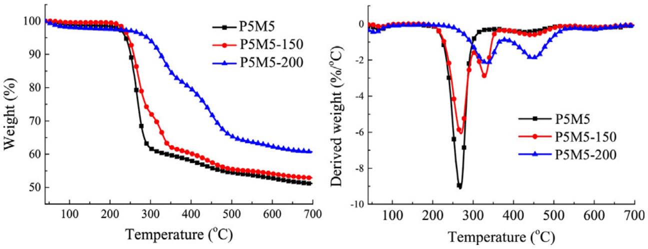

Fig. 3. TGA weight loss and corresponding DTG curves for P5M5, P5M5-150 and P5M5-200 aerogels.

Table 2
TGA parameters of the resulting aerogels in the N_2 atmosphere.

Samples	$T_{d5\%}$ (°C)	T_{dmax} (°C)	dW/dT (%/min)	Residue (%)
P5M5	239.0	268.5	9.15	51.14
P5M5-150	246.1	270.2	6.08	52.87
P5M5-200	292.4	332.1	2.17	60.67