

THERMAL DEGRADATION AND FLAME RETARDANCY OF CALCIUM ALGINATE FIBERS*

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Abstract Calcium alginate fibers were prepared by wet spinning of sodium alginate into a coagulating bath containing calcium chloride. The thermal degradation and flame retardancy of calcium alginate fibers were investigated with thermal gravimetry (TG), X-ray diffraction (XRD), limiting oxygen index (LOI) and cone calorimeter (CONE). The results show that calcium alginate fibers are inherently flame retardant with a LOI value of 34, and the heat release rate (HRR), total heat release (THR), CO and CO₂ concentrations during combustion are much lower compared with those of viscose fibers. Calcium carbonate and calcium oxide were formed during thermal degradation of calcium alginate fibers at different temperatures. The shape of calcium alginate fibers is well kept after LOI test. The rigid combustion residue char acts as an effective barrier to the outward diffusion of flame and heat. The combustion process and flame retardant mechanism of calcium alginate fibers are also discussed.

Keywords: Calcium alginate fiber; Flame retardancy; Wet spinning; Combustion process; Thermal degradation.

INTRODUCTION

Upholstered furniture and furnishings play an important role in our daily life to make life more comfortable. However, statistics shows that more than 94% of the fire fatalities occurred in dwellings and that a major cause of fire fatalities in dwellings was associated with burning of upholstered furniture. Textile flame retardancy is highly demanded in work clothing, firefighter apparel, institutional draperies, institutional upholstery, institutional and commercial carpet, transportation, military garments, and bedding^[1]. Research on fibers and textiles having inherent flame retardancy has received considerable attention recently^[2, 3]. A number of synthetic fibers with good flame retardancy property have gained increased usage including melamine-based fibers, viscose rayon containing silica acid^[4], aramides and oxidized polyacrylonitrile fibers. However, there is much less work on inherent flame retardant fibers produced from natural resource.

Alginate is a naturally occurring linear polysaccharide extracted from brown seaweed. It is composed of 1-4 linked α -L-guluronic (G) and β -D-mannuronic (M) acid residues. Like cellulose, it acts as a reinforcing element in cell walls of brown seaweeds^[5]. Alginate is one of the most abundant biodegradable and sustainable natural resources in the world and is widely used in the textiles, food, and chemical industries as a thickening and gelling agent. More than fifty percent of alginate is produced in China. Fibers that made from alginate salt are biodegradable and can be used in making clothes, decorating materials and medical textiles. Unlike most

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synthetic fibers produced from petrochemical resources, such as polyester, acrylic and polypropylene fibers, the raw materials of alginate fibers is from brown seaweed which is a rich ocean resource. With the use of aqueous spinning solution and water bath containing calcium chloride to coagulate, the spinning process for alginate fibers is totally green without any use of toxic or organic solvents^[6, 7]. Recent increase in demand for oil, associated with price increase and environmental issue is continuing to exert pressure on an already stretched world energy infrastructure. As renewable and biodegradable materials, calcium alginate fibers have a broad prospect in applications. However the flame retardancy and combustion process of calcium alginate fibers have not yet been reported. In this article, calcium alginate fibers are prepared, and the thermal degradation, flame retardancy of calcium alginate fibers are investigated. Flame retardancy mechanism and combustion process of calcium alginate fibers are discussed. Viscose fiber, which was common used in textile and has similar structure units with alginate, is used for combustion comparing with calcium alginate fibers.

EXPERIMENTAL

Materials and Reagents

Sodium alginate powder (120 mPa·s) was purchased from Qingdao Mingyue Company. For comparison purposes, viscose fiber (1.67 dtex × 38 mm), obtained from Shandong Helon company, was used for flame retardancy tests. Other reagents were all commercially available analytical grade and used as received.

Preparation of Calcium Alginate Fibers through Wet Spinning

Solutions of sodium alginate of 5.0 wt% concentration was prepared and made completely homogeneous with demineralised water under high speed stirring, and then filtered through a 20 μm PP filter membrane under vacuum^[6]. The filtrate was left to stand still until trapped air bubbles were removed. The solution was then extruded from a viscose-type spinneret into a coagulating bath containing 4.5 wt% CaCl₂ aqueous solutions to form fibers. The obtained calcium alginate fibers were washed free from spin bath liquor in a conventional wash system, dried and stretched in a steam chamber. After that, the obtained calcium alginate fibers were cut into short fibers having 38 mm in length.

Characterization

The mechanical properties of the fibers were measured by a Favimat-airobot single fiber testing machine made by Textechno Company.

The thermal degradation property of calcium alginate fibers was analyzed by using a TGA 2050 (TA Instruments Company) with heating rate 10 K/min under air condition. Calcium alginate fibers were heated to 150°C, 420°C, 500°C and 700°C, respectively and kept for 2 h with heating rate 10 K/min under air condition in a tube furnace. And the thermal degradation products were investigated with a Rigaku D/max-2500 X-ray diffractometer (XRD).

The scanning electron microscopy (SEM) images of combustion residues after LOI tests were obtained by a JEOL JSM-6390LV scanning electron microscope. The specimens were coated with a conductive layer of gold.

Limiting oxygen index (LOI) measurements were carried out using a JF-3 type instrument (made in Nanjing Jiangning Analytic Instrument Company) in accordance with GB/T 5454-1997.

The combustion behavior of fibers was studied using an FTT Dual Cone Calorimeter (CONE), made by Fire Testing Technology Limited, under fully ventilated conditions. The testing procedures followed the ISO 5660-1 standard, and the external heat flux level was set at 50 kW/m². For testing, the fibers were cut into 38 mm and hot pressed into 4 mm thick 100 mm × 100 mm plaques which were then encased in an aluminum foil exposing to top surface, mounted in a stainless steel holder and with a grid placed on top of the sample. Tests were conducted in triplicate, and standard deviations are indicated by the error bars on particular regions of the graphs.

RESULTS AND DISCUSSION

Mechanical Properties of Calcium Alginate Fibers

The strength of a fiber is one of the key factors affecting the applications of fiber materials. Calcium alginate

fiber has been studied for many years, but its strength was not strong enough for the use in textile and fabrics^[8]. By using multi-stage drawing process, calcium alginate fibers with homogenous structure and tenacity higher than 2.42 cN/dtex could be obtained. Compared to short-staple viscose fiber and cotton, the strength of which was about 1.6–2.5 cN/dtex, the acquired calcium alginate fibers were strong enough to be used in making textile fabrics.

Thermal Degradation of Calcium Alginate Fibers

The thermal degradation curve of calcium alginate fibers under air condition is shown in Fig. 1. We can see from the curve that calcium alginate fibers have good thermal stability. The thermal degradation residue is 12.5% of original fiber at 900°C. The weight loss from room temperature to 200°C is caused by the dehydration of calcium alginate fibers. In order to study the thermal degradation process, the thermal degradation products of calcium alginate fibers after heat treated in tube furnace were analyzed with XRD, and the results are shown in Fig. 2. It is very interesting to find that calcium carbonate was formed when calcium alginate fibers were heated to 150°C, and calcium oxide and calcium hydroxide were found when heated to 700°C as shown in Fig. 2. The formation of calcium carbonate at low temperatures probably plays a key role for the flame retardancy of calcium alginate fibers.

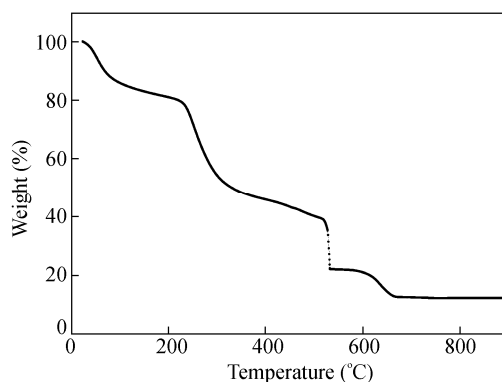


Fig. 1 Thermal degradation curve of calcium alginate fibers with heating rate 10 K/min under air condition

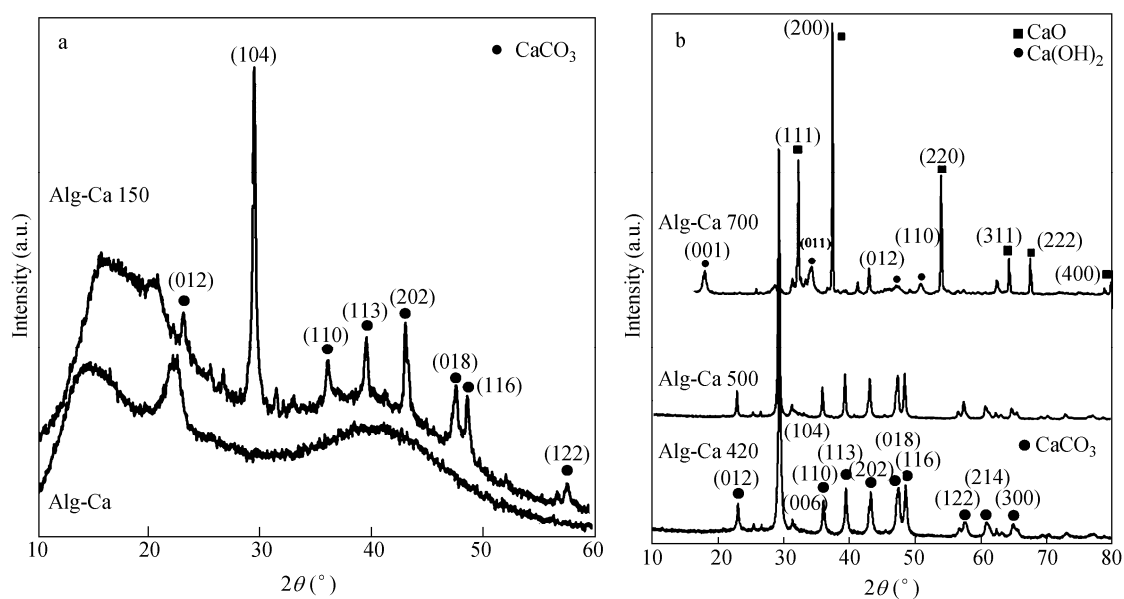


Fig. 2 XRD curves of thermal degradation products of calcium alginate fibers (Alg-Ca) at 150°C, 420°C, 500°C and 700°C, respectively

Flame Retardancy of Calcium Alginate Fibers

The values of LOI measure the minimum concentration of oxygen required to sustain the combustion of a material and is the simplest method to measure the flammability of materials. The LOI values of calcium alginate fibers and viscose fibers are 34 and 17 respectively. It shows that calcium alginate fibers are inherent flame retardant materials, and viscose fibers are flammable. Compared to viscose fibers, calcium alginate fibers can be fabricated into textiles which can be used in strict flame retardation regulation field.

A number of properties can simultaneously be determined in a cone calorimetry test. Combustion parameters of calcium alginate fibers and viscose fibers from cone calorimetry measurements at 50 kW/m^2 are shown in Figs. 3(a)–3(d).

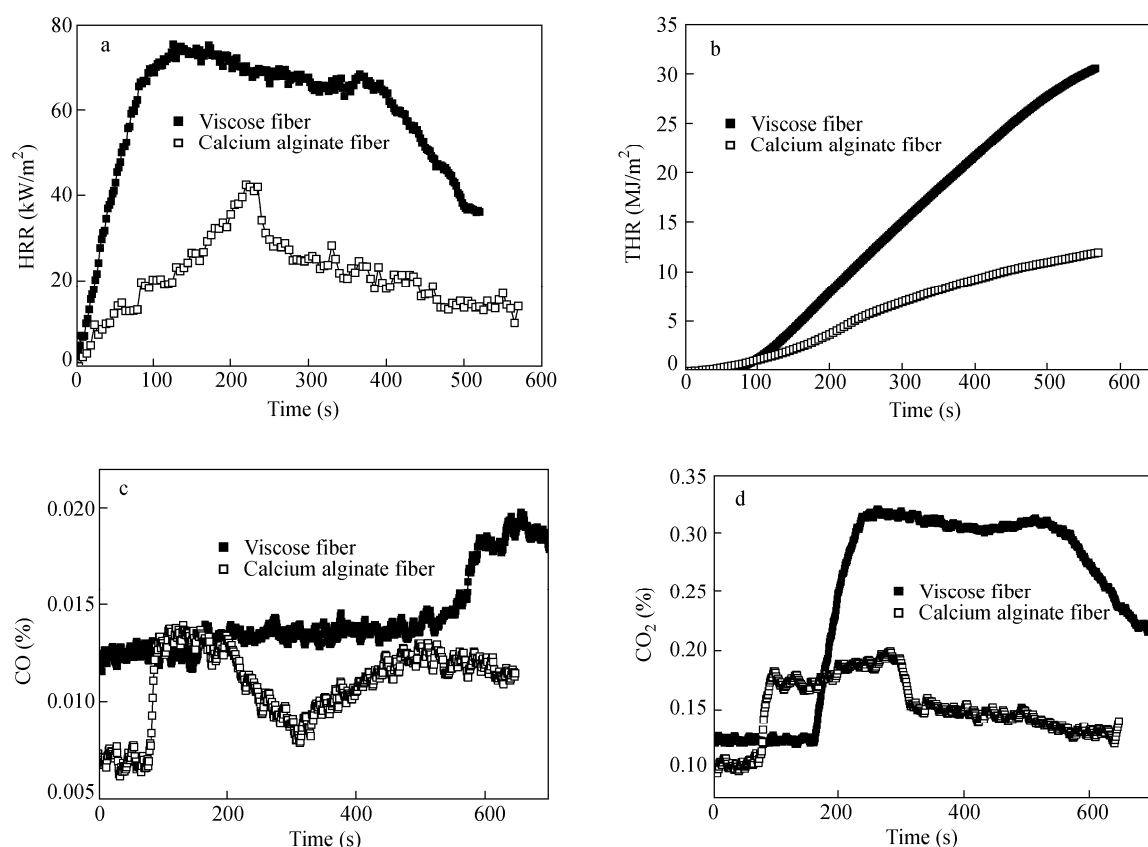


Fig. 3 Combustion parameters of calcium alginate fibers and viscose fibers from cone calorimetry measurements at 50 kW/m^2
a) Heat release rate (HRR) curves; b) Total heat release (THR) curves; c) CO concentration; d) CO₂ concentration curves

The most important parameters are the time to ignition (TTI) and heat release rate (HRR), as these may relate to fire growth and toxic gas emission on burning^[9]. The TTI is described as the time to achieve sustained flaming combustion at a particular irradiance. According to CONE measurements, the TTI values of viscose fibers and calcium alginate fibers are 5 s and 26 s respectively. Therefore, calcium alginate is hard to ignite and is very safe for textile use. The shape of the HRR curve over time is considered important as it may reveal information on the changing behavior of the burning process and the effect of various factors being investigated^[10]. Figure 3(a) shows the HRR of the viscose fibers and calcium alginate fibers after ignition. The results show that the heat release of viscose fibers increases in less than 100 s after ignition to a high level about

50 kW/m² and maintains at that level for about 300 s, while the HRR of calcium alginate fibers increases slowly and maintains at about one third of that of viscose fibers. The total heat release (THR), as shown in Fig. 3(b), also indicates that heat release of calcium alginate fibers during combustion is very small and not enough to sustain combustion without the external heat flux.

The CO and CO₂ concentrations obtained from the measurement of exhaust gas during combustion, as shown in Figs. 3(c) and 3(d), reveal that the inherent flame retardant calcium alginate fibers yield much less CO and CO₂, compared to viscose fibers, during combustion. The evolution and concentrations of CO and CO₂ during combustion are very important to assess the safety of fire because most victims during fire are caused by inhalation of great amounts of CO and CO₂. The much lower CO and CO₂ concentrations during combustion of calcium alginate fibers are obviously advantageous over most flame retardant materials where the releases of CO and CO₂ are much higher after flame retardation modification^[11, 12]. The excellent flame retardancy properties of calcium alginate fibers are probably caused by the existing of carboxylic groups and calcium ions in calcium alginate structure units that promotes dehydration reaction and decarboxylation reaction to release non-burning gases, such as H₂O and CO₂.

Combustion Process and Char Formation Analysis

The weight loss and derivate weight loss curves of viscose and calcium alginate fibers during combustion are shown in Figs. 4(a) and 4(b). It can be seen that the combustion residue of calcium alginate fibers is about 25%, much higher than that of viscose fibers (9%). The high amount of combustion residue also indicates the flame retardancy of calcium alginate fibers^[13]. According to the curves of derivate weight loss during combustion, we can divide the combustion process of viscose fibers and calcium alginate fibers into three and four stages, respectively.

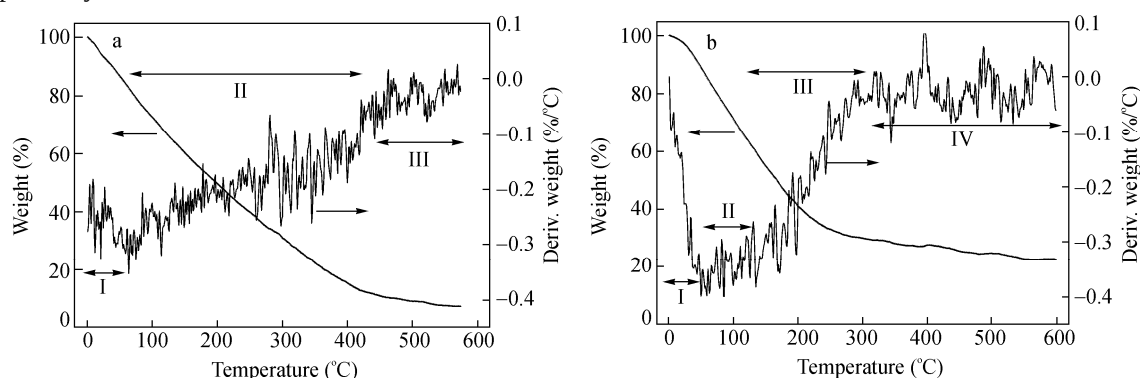


Fig. 4 Weight loss and derivative weight loss curves from cone calorimetry measurements at 50 kW/m²
a) Viscose fibers; b) Calcium alginate fibers

The combustion process of the viscose fibers is shown in Fig. 4(a). Stage I shows the process of intermolecular and intramolecular water loss of the fibers. Stage II reveals the process of fierce pyrolysis and combustion which is in agreement with the curve of HRR. During this stage, viscose fibers undergo transglycosylation and cross-linking reactions leading to the formation of an intermediate compound laevoglucosan which subsequently decomposes into volatile flammable compounds and burns vigorously. Stage III shows the combustion process of the residue materials, during this process the weight loss rate is decreased.

Figure 4(b) shows the combustion process of calcium alginate fibers. Since calcium alginate fibers are hydrophilic, stage I shows the quick loss of water and the formation of calcium carbonate upon heating which favors flame retardancy. During stage II, calcium alginate fibers decompose rapidly and small molecules are released, but the amount of flammable decomposition products is low, the HRR maintains at low level; during stage III small amount of combustible compounds are released from burn of calcium alginate fibers; and stage IV reveals the weak combustion and degradation of residue materials, such as calcium carbonate and calcium oxide.

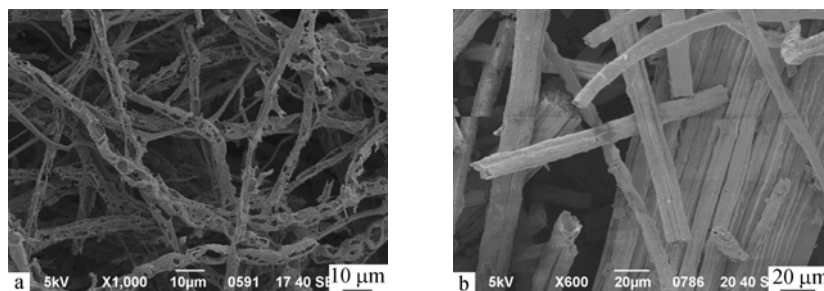


Fig. 5 SEM images of combustion residue from cone calorimetry measurements at 50 kW/m²
a) Viscose fibers; b) Alginate calcium fibers

The combustion residues of viscose fibers and calcium alginate fibers after LOI tests were analyzed with SEM and shown in Figs. 5(a) and 5(b). The shape of the fibers was well kept in the case of alginate fibers, while that of viscose fibers after combustion was highly porous. The combustion residue of alginate fibers was rigid and in big amount, while that of viscose fibers was brittle and in small amount. Van Krevelen^[14] studied char formation in a number of polymers and showed that the inherent flammability of polymers reduces as their char-forming tendency increases. Preferential formation of the combustion residue in the case of calcium alginate fibers not only reduces the production of flammable volatiles but also maintains a coherent flame and heat barrier between igniting sources and underlying materials. This could be one of the reasons for the flame retardancy of alginate fibers.

CONCLUSIONS

Calcium alginate fibers having good tensile strength were obtained through a wet spinning technique. Calcium alginate fibers, which have excellent fire performance, were inherent flame retardant. The high yield char residue was rigid, and the shape of calcium alginate fibers was well kept after combustion. The presence of carboxylic groups and calcium ions in calcium alginate structure units could promote dehydration reaction and decarboxylation reaction, and hence makes calcium alginate fibers inherent flame retardant. The formation of calcium carbonate during thermal degradation at low temperatures probably plays a key role for the flame retardancy of calcium alginate fibers. It is worthy to do more research considering the huge potential commercial use in the future.

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