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Nanoporous SiO_2 grafted aramid fibers with low thermal conductivity

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ABSTRACT

Silica aerogel is an excellent thermal insulation material for its mesoporous nanostructures In this study, the aramid fibers were grafted with the mesoporous structure of silica aerogel to reduce the fiber thermal conductivity through a serious process. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) results indicate that siloxane groups were successfully grafted onto the fiber surface through nitration, reduction and grafting with 3-glycidoxypropyltrimethoxysilane (GPTMS). After cohydrolysis with tetraethyl orthosilicate (TEOS), condensation, alkylation and ambient drying, SEM images of the as-prepared fibers showed that a mesoporous structure formed around the fiber surface. Si content within the as-prepared fiber was about 10.5 times higher than the fiber grafted with GPTMS. The fiber was covered with a mesoporous and hyperbranched network. As a result, the thermal conductivity of blanket consisting of the as-prepared aramid fibers, measured by transient hot-wire method, was obviously lower than that of the original ones, whereas the thermal stability changes little.

1. Introduction

Silica aerogels are low-density, translucent and thermal-insulating material consisting of nanoparticle building blocks, networked together to form an open, highly porous structure. They have large surface area (500–1500 m^2/g), high porosity (80–99%), and low bulk density (0.03–0.35 g/cm^3). Silica aerogels have attracted much attention for they have a large potential to be applied in many fields, considering the uncommon properties mentioned above [1–3]. Silica aerogels are produced by removing the entrapped solvent from a wet gel while maintaining the integrity and high porosity of the gel. Tetraethylorthosilicate and methyltrimethoxysilane based silica aerogels have been synthesized under ambient pressure drying or supercritical drying through sol-gel method [4–6]. However, silica aerogels are not routinely found in our daily life as their mechanical properties are not good enough to be directly applied.

Excellent integrated performances, especially super fatigue resistance, high strength and good thermal resistance, make aramid fibers one of the best choices meeting the harsh requirements of many cutting-edge fields including space and aviation, electronics, tanks, bulletproof products [7–10]. To optimize the specific engineering applications, many types of aramid fibers have been developed, such as Kevlar 29 and Kevlar 49. Aramid fibers, which have low thermal conductivity, are widely used as a functional material for thermal protection in firefighters' protective clothing [11]. However, current aramid fibers serving as a thermal barrier in firefighter protective clothing cannot provide enough thermal protection during firefighting [12]. To improve thermal-insulation ability, aramid fibers need surface modification. However, the highly crystalline molecular chain structure oriented along the fiber axis results in chemical inertness of the fiber [13]. Many efforts have been made to overcome the smooth surface and inertness of aramid fibers including dipcoating [14], chemical etching [15], chemical grafting [16–18], plasma modification [19] and γ-ray irradiation [20]. However, chemical etching seriously harms the structures and mechanical properties of aramid fibers. Plasma modification and γ-ray irradiation can graft some certain functional groups (ie. nitrogen-containing or oxygen-containing functional groups) to the aramid fiber surface. Nevertheless, special and expensive facilities are needed to realize plasma modification and γ-ray irradiation, besides, which can also promote aging behavior [17]. Chemical grafting has often been utilized because of its great potential in achieving expected performance by adjusting the types of grafting functional groups. Ai et al. [13] grafted

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alkoxysilane onto the surfaces of Kevlar fibers, where the surface area was enlarged about 10 times and the adhesion between the fiber and the resin matrix was markedly improved. Zhang et al. [17] have grafted hyperbranched polysiloxane to the aramid fiber surface to improve UV resistance, surface activity, thermal and mechanical properties. So far, however, chemical grafting has mainly focused on grafting some small-molecule or hyperbranched macromolecule compounds on to the surface of aramid fibers to improve the surface properties including adhesion ability with resin, surface activity, mechanical property and UV resistance [13,21]. Researchers studying chemical grafting onto aramid fibers have seldom considered improving the fibers' thermal conductivity to meet the need in emergency situations such as firefighting.

Silica aerogels are nanoscale mesoporous light materials with extremely low thermal conductivity (0.01–0.03 W/mK) prepared through sol-gel method [22]. The sol-gel process has long been used to modify cellulose fibers to reduce the fibers' moisture adsorption capacity, improve the mechanical properties and so on [23–26]. The sol-gel method, using TEOS as precursor, is used to form SiO_2 nanoparticles attached to the surface of cellulose fiber. However, the SiO_2 nanoparticles do not form the networked, highly porous structure, but just discretely distributed onto the fiber surface. The thermal conductivity cannot be reduced under this circumstance and considerable work should be done.

Recently we have successfully synthesized nanostructured and highly porous silica aerogels using TEOS [27]. Following our advances in this field, we present here a study that aims to reduce the thermal conductivity of aramid fibers through surface modification. Siloxane groups were grafted onto the fiber surface, and then highly porous and nanostructured network formed around the fiber surface by means of sol-gel process.

2. Experiments and characterization

2.1. Materials

Kevlar 29 fibers were made by DuPont Company, Wilmington, DE. The silane coupling agent γ-(glycidyloxypropyl)trimethoxysilane (GPTMS) of analytical grade was purchased from Aladdin Reagent. Other reagents were all of analytical grade and made by Sinopharm Chemical Reagent Co., Ltd, China. All the reagents were used as received.

2.2. Preparation of amino Kevlar fibers

Kevlar 29 fibers were immersed in acetone and deionized water in sequence and then heated to reflux temperature for 3 h to eliminate organic impurities on the fiber surface. The fibers were then dried in a vacuum oven at 80 °C for 6 h to obtain clean fibers, which are denoted as KFs. Nitrification medium was prepared by blending four acids in a volume ratio of 40:2:370:100 (fuming nitric acid/concentrated sulfuric acid/acetic anhydride/glacial acetic acid). The reducing agent (0.55 g of sodium borohydride) and the buffer reagent (0.12 g of potassium dihydrogen phosphate and 0.36 g of dipotassium hydrogen phosphate) were dissolved in a 200 mL tetrahydrofuran to form a restoring medium. KFs were immersed in the nitrification medium at 45 °C for 24 h, washed with deionized water, and then dried. Then, the fibers were reduced by the restoring medium at room temperature for 24 h. The resultant fibers were pretreated fibers, which have amino groups, and are denoted as aKFs.

2.3. Grafting siloxane groups

One gram of aKFs, 40 mL EtOH and 5 mL GPTMS were placed into a beaker and stirred for 5 min using magnetic stirrer. Then the beaker was placed into 45 °C water bath for 12 h. The resultant fibers were grafted with siloxane groups and are denoted as g-aKFs.

2.4. Sol-gel and surface modification

The g-aKFs were washed with ethanol twice and then mixed with 11.5 mL TEOS and 30 ml EtOH in a beaker. 4 ml deionized water and 800 μL 0.1 M HCl were subsequently added to the beaker. They were stirred for 10min and then placed into 45 °C water bath for 12 h. Then 1200 μL 0.5 mol/L NH_4OH were dropped to the system. They were vigorously stirred for 5min, and the liquids were poured out of the beaker. The wet fibers gelled within 10 min. After gelation, the fibers were immersed in EtOH and placed into 45 °C water bath for 12 h to age. Then, *n*-hexane was used to exchange EtOH in 12 h. 15 vol% trimethylchlorosilane (TMCS)/n-hexane solution was used to modify the fiber in 12 h. All the exchange and modification process were conducted in 45 °C water bath. Finally the modified fibers were dried under 60 °C for 2 h and then 90 °C for 6 h.

The fibers with nanosized and highly porous surface can be obtained which is denoted as s-g-aKF.

2.5. Characterizations

The surface chemical modification of the aerogels was studied

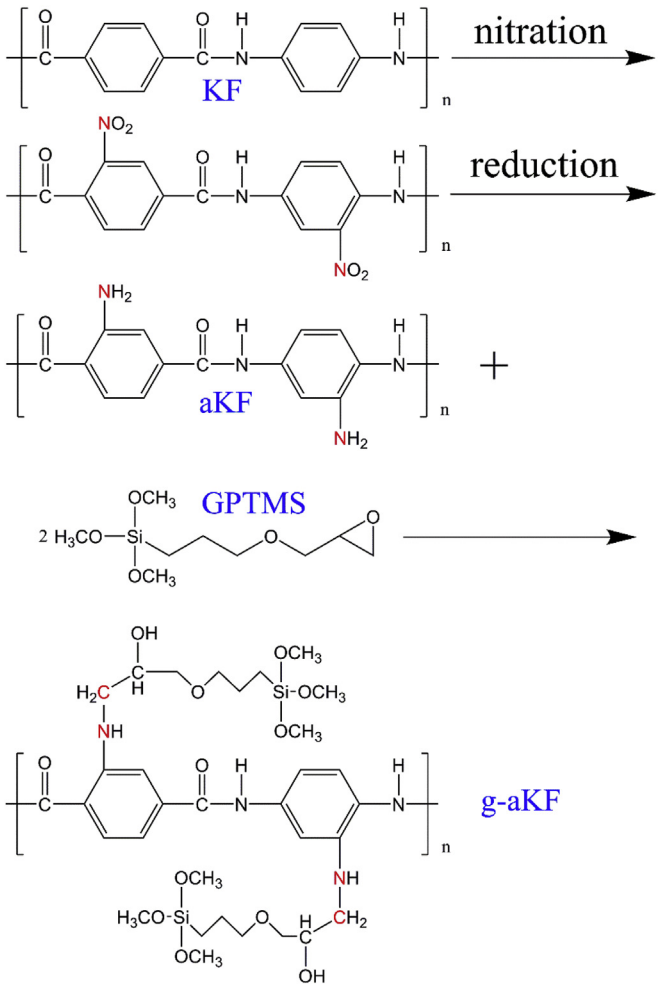

Fig. 1. Mechanism for preparation of g-aKF.