THERMAL PROPERTIES OF ELECTROSPUN NANOFIBERS WITH AEROGEL

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Abstract

Textiles perform an important function of protecting humans from extreme conditions. For this function, the efficacy of the fabric is a very important parameter. To improve the thermal properties of textiles, different fabrics and coating materials need to be evaluated. The thermal properties of nanofibers and their potential protection against cold environments are relatively unknown. It is possible to decrease the weight and bulk of current thermal protective clothing by incorporating nanofibers in thermal insulation battings. Such a modification will also increase the mobility of the wearer. In this paper, the mechanisms of heat transfer through fibrous insulation where the fiber diameter is less than 1 micrometer (μm) was evaluated. Using electrospinning process, flexible electrospun PUR and PVDF nanofibers embedded with silica aerogel was produced. A detailed study of thermal properties of the electrospun nanofiber embedded with SiO_2 aerogel was conducted. The microscopic examination confirmed presence of aerogel. The results were statistically analyzed. The samples showed enhancement of thermal insulation by increasing the number and the weight per unit area of both nanofibrous layers. The results also confirmed that embedding silica aerogel in nanofibrous layers leads to increased thermal insulation. Based on the results, nanofibers embedded with aerogel were found to be good for thermal insulation at extreme conditions.

Keywords: Nanofiber, aerogel, thermal Insulation, conduction, heat transfer

1. INTRODUCTION

Electrospinning is a simple and low-cost method for making polymer and ceramic fibers with superfine diameters [1-3]. In recent years, it has attracted an increasing interest in the electrospinning technique owing to the promising properties of the electrospun nanofibers. Various structured and assembled nanofibers have been developed via electrospinning. Recent advances in the technology of producing nanofibers have revealed a gap in our knowledge about the heat transfer behaviour of low-density nanofibrous layers. Understanding heat transfer through nanofiber structures will allow us to exploit the unique properties of polymer nanofibers for applications such as improved military cold weather clothing and hand wear, sleeping bags, and tent liners, as well as applications for military food service refrigeration and storage equipment [4]. Silica aerogel is a highly porous material with pore diameters in the range of 2-50nm [5, 6].

The nanoporous structure of the silica aerogel having a high porosity above 90% makes the aerogel a highly thermal insulating materials with a super-low thermal conductivity as low as $0.013 Wm^{-1}K^{-1}$. Silica aerogel has well been acknowledged as one of the most attracting thermal insulation materials for wide applications in aircrafts and aerospace, chemical engineering, building constructions, and so forth [7-9]. Heat transfer through porous media consists of conduction, convection, and radiation. Many practical applications focus on fibrous materials that have a low fiber volume fraction (less than 10% fiber for the most part). Lightweight and compressible insulation materials maximize insulating value at a minimum weight. For these types of materials, heat conduction through the solid portion of the matrix (fibers) is negligible, so it is not necessary to focus on solid conduction heat transfer. However, conduction through the still air trapped within the insulation is important, and the thermal conductivity of air, total gas volume fraction, and thickness of air within the material is required to properly analyse both radiation heat transfer and convection heat transfer mechanisms [4]. Literature searches on the subject of submicron fibers in thermal insulation reveal no fundamental or applied work using polymer nanofibers for thermal insulation applications. In this paper, we addressed the mechanisms of heat transfer through fibrous insulation where the fiber diameter was less than 1 micrometer (μm). The thermal insulating efficiency of fiber-based insulation is known to increase as the fiber size is reduced. Flexible electrospun nanofibrous layers embedded with silica aerogel was produced via electrospinning process. The electrospun PUR and PVDF nanofibrous microstructures were fabricated and then used to reinforce the SiO_2 aerogel. The effects of thermal properties of the electrospun nanofibrous layers embedded with SiO_2 aerogel were evaluated.

2. MATERIALS AND METHODS

2.1. Materials

Silica aerogel powder and granules were purchased from Cabot aerogel Corp. Polyurethane (PUR) & PVDF was used from the CXI lab (nanocenter, TUL, Czech Republic). The samples were electrospun PUR & PVDF nanofibrous layers embedded with silica aerogel. The samples were of different types of Aerogel nanofibrous layer with and without Spunbond PP back up that contained only PUR/PVDF or with Aerogel granular powder.

2.2. Methods

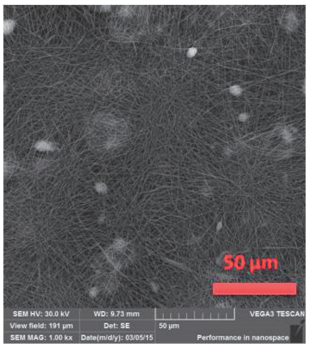
2.2.1. Electrospinning of PVDF & PUR nanofibrouslayers

The polyurethane (PUR) was dissolved in Dimethylformamide (DMF) at room temperature at a concentration of 18 wt.% (g/mL) and at the same concentration of PVDF also was first stirred for 2 hours and then with SiO_2 aerogel in both powder and granule forms were added. These mixtures were stirred for 1-2 hours at room temperature prior to electrospinning and were then electrospun at room temperature. The prepared solution was placed in a cylinder containing active electrode parallel to collecting electrode. The fibers were collected on a spunbond polypropylene fabric. The electrospun PUR and PVDF nanofibrous layers embedded with silica aerogel have been investigated on their morphology and microstructure by using a SEM (VEGA TESCAN Inc. USA) at 30 kV. The densities of the samples were determined by measuring the weight and volume.

To investigate the comparative thermal properties of insulating materials, alambeta instrument developed at the Technical University of Liberec, Czech Republic was used. Electrospinning was carried out using “Nanospider” technology as a modified electrospinning technique, Nanospider laboratory machine NS LAB 500S from Elmarco s.r.o. Electrospinning is widely accepted as a technique to fabricate submicron polymer fibers. Nanospider technology allows the production of nanofibers from polymers dissolved in water, acids or bipolar solvents as well as from melted polymers and is suitable for the production of organic and inorganic fibers. This versatile technology is easily adapted to a variety of process parameters for the optimization of the specific properties of the produced nanofibers [10-13]. The innovatory idea of the Nanospider is based on the possibility of producing nanofiber from a thin layer of liquid polymer. In this case, Taylor cones (the source of nanofiber) are created on the surface of a rotating roller, immersed in a polymer solution. Because the Taylor streams are formed next to each other, throughout the entire length of the roller, this revolutionary idea produced many advantages, such as high productive ability. This commercial method for production of polymeric nanofiber is used in industrial range. This is a simple and versatile method for production of ultrathin fibers from a variety of materials that include polymers. In addition, Nanospider has the ability to process a wide range of polymers in diameters of 50-300 nm into nonwoven webs [14]. One way ANOVA was used to analyse the experimental data.

3. RESULTS AND DISCUSSION

Figures 1 and **2** show the morphologies and microstructures of electrospun PUR & PVDF nanofibrous layers. The electrospun nanofibrous layers have better integrity and flexibility. The different microstructures could be observed with and without aerogel particles present which were electrospun from the solutions with the concentration of 18wt.%.

PUR 1


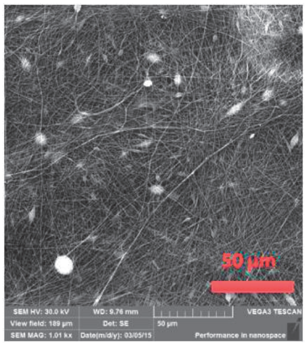
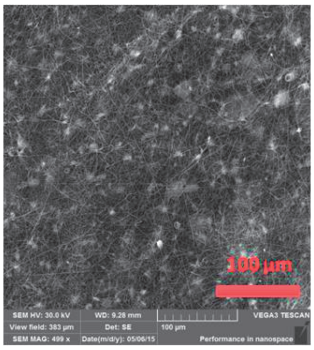
PUR 2


Figure 1 Morphology and microstructure of electrospun PUR nanofibrous layers embedded with SiO_2 aerogel from 18 wt.%

PVDF 1


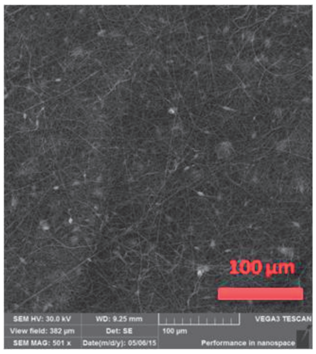
PVDF 2


Figure 2 Morphology and microstructure of electrospun PVDF nanofibrous layers embedded with Silica aerogel from 18 wt.%

Thermal conductivity as a function of areal density for PUR and PVDF electrospun nanofibrous layer embedded with silica aerogel is shown in the **Figure 3**. As shown in the **Figure 3**, thermal conductivity of the electrospun nanofibrous layer decreased with increase in density. This can be explained by the fact that as the density increases; it makes the fibrous structure more packed. This causes the mean free path (distance travelled by a photon before it collides with another fiber surface [15] for a photon movement to decrease thus causing a decrease in the heat transfer because of radiative conduction. When the density comes to a critical point, the increase in conduction through solid phase (fibers) and decrease in radiation conductivity results in an increase in total thermal conductivity [16, 17].

In fact, in fibrous structures the small size of the pores and the tortuous nature of the air channels present prevents any heat transfer by convection [20] Moreover, in fibrous insulation materials because of low fiber volume fraction, heat conduction through the solid phase (the fibers) is not significant and conduction through air is usually considered to be the conductivity of still air that is poor at room temperature. Thus, radiative conductivity is the prevalent mechanism of conductivity since it has a high porosity percentage of fibrous structures. By adding a nanofiber web, thermal conductivity was enhanced noticeably that is believed to be because of their extremely fine fiber and very high porosity of web. The superfine fibers in the web have better radiation absorption and extinction since their higher surface-area-to-volume ratio leads to decrease in the thermal conductivity. Moreover, smaller pore size between nanofibers decreases the mean free path for photon movement resulting in lower radiative energy transfer. This improvement becomes more significant when bulk density is increased. In high densities, increase in the thermal conductivity of the sample containing web was diminished which may be attributed to the presence of nanofiber and their natural compact structure that could compensate for increased thermal conductivity.

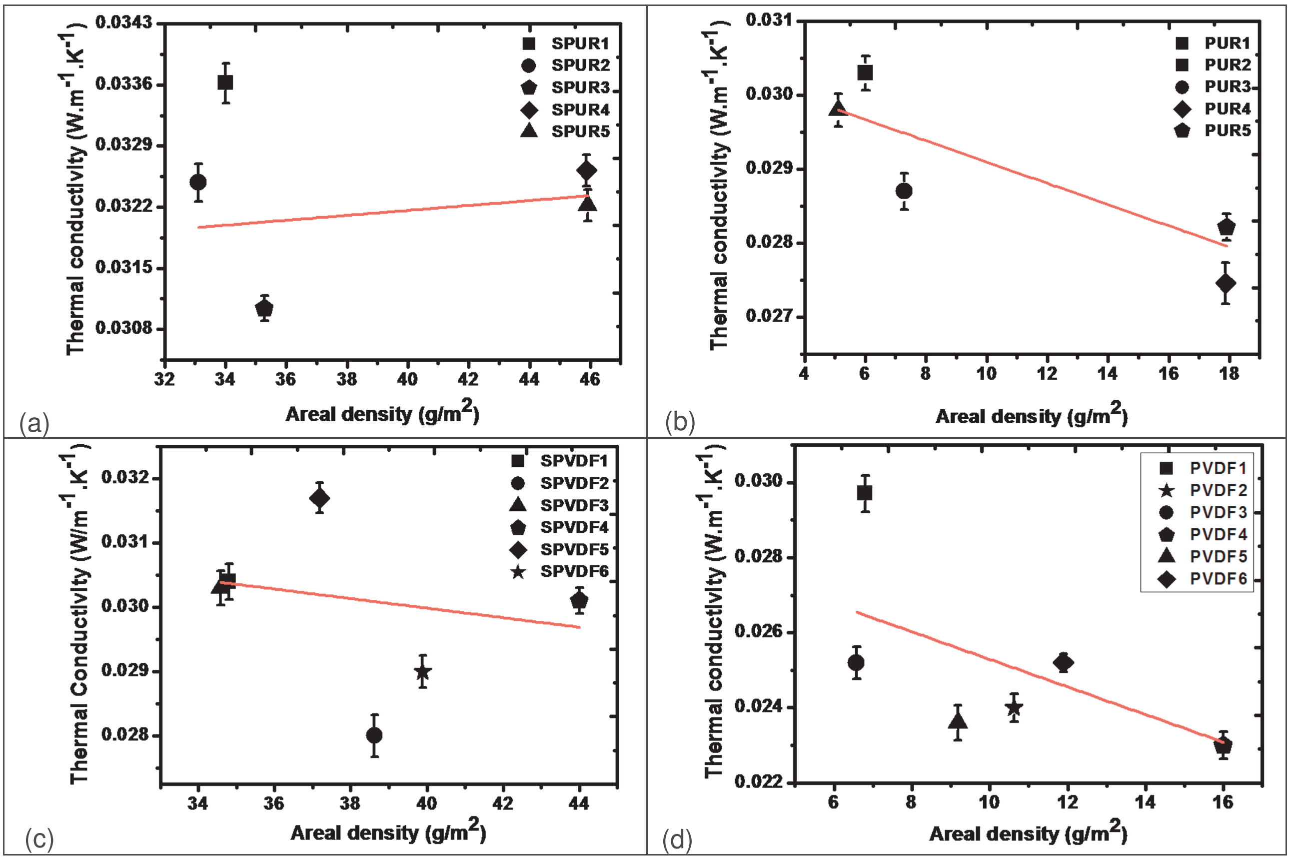


Figure 3 Thermal conductivity Vs GSM for (a) PUR samples with spunbond PP; (b) Electrospun PUR nanofibrous layers embedded with aerogel; (c) Electrospun PVDF nanofibrous layers embedded with aerogel backed up with spun bond PP and (d) Electrospun PVDF nanofibrous layers embedded with aerogel

According to thermal conductivity curves which is apparent in **Figures 3**, decrease in the average nanofiber diameter leads to lower limit of conductivity. Higher specific surface of thinner fibers [18] means more surface area for radiative absorption resulted in lower thermal conductivity. Further, higher porosity of the web with a nanofiber diameter around 150 nm could be the other reason for their lowest thermal conductivity. Another explanation for reduction in conductivity can be smaller pore size in the web containing thinner nanofibers leading to lower radiative conductivity. In this context, it could be understood that using thinner nanofibers leads to noticeable performance and helps in achieving very low limit of thermal conductivity. Of particular interest are the results for the two nanofiber insulation materials (electrospun PUR and PVDF nanofibrous layer). Both materials showed excellent reduction in overall heat transfer compared to standard low-density fibrous insulating materials (at areal densities above 40 g/m^2).

The PVDF nanofibrous layer, in particular, showed superior insulation at higher areal density values. Thermal conductivity testing confirmed that decreasing fiber diameter tends to increase the thermal resistance of fibrous insulation materials. However, the nanofiber/aerogel becomes an effective insulator since the aerogel structure suppresses conduction and convection, and the fibers reduce radiation heat transfer while increasing the strength of the brittle and weak aerogel structure. Although the aerogel/nanofiber combination has good thermal properties, the volume fraction of fiber must be fairly high to support and protect the aerogel matrix.

Thus the aerogel materials can't achieve the same thermal conductivity at densities as fibrous insulation, but they do achieve better thermal resistance for an equivalent thickness of material. High porosity of electrospun fibrous mesh is able to trap air which potentially gives it a good thermal insulation property. This is confirmed using thermal conductivity tests which show that decreasing fiber diameter leads to an increase in thermal resistance. With respect to high porosity fibrous insulation materials, aerogel/nanofiber has excellent insulation per unit thickness properties, as shown in **Figure 4**. From the figures, it can be seen that the thermal resistance increases with the increases in thickness. Also, the electrospun PVDF nanofibrous layer embedded with silica aerogel is higher than electrospun PUR nanofibrous layer embedded with silica aerogel.

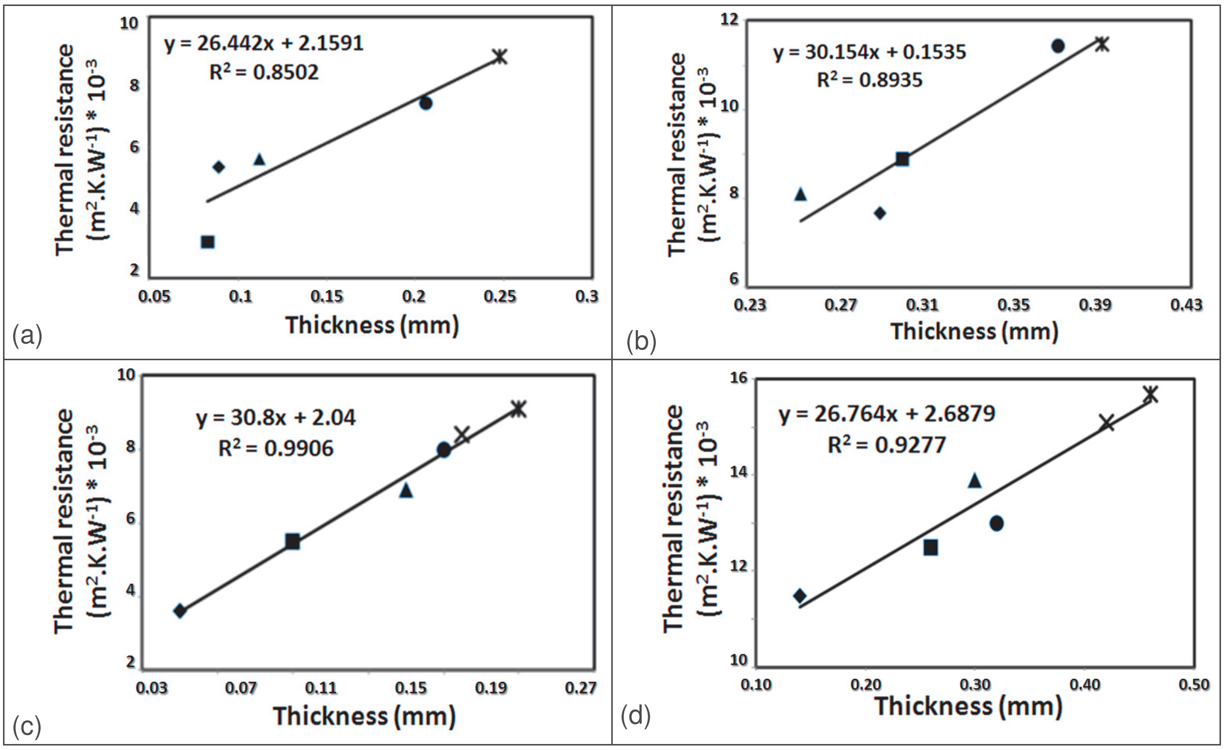


Figure 4 Thermal resistance Vs Thickness (a) PUR samples with spunbond PP; (b) Electrospun PUR nanofibrous layers embedded with aerogel; (c) Electrospun PVDF nanofibrous layers embedded with aerogel backed up with spun bond PP and (d) Electrospun PVDF nanofibrous layers embedded with aerogel

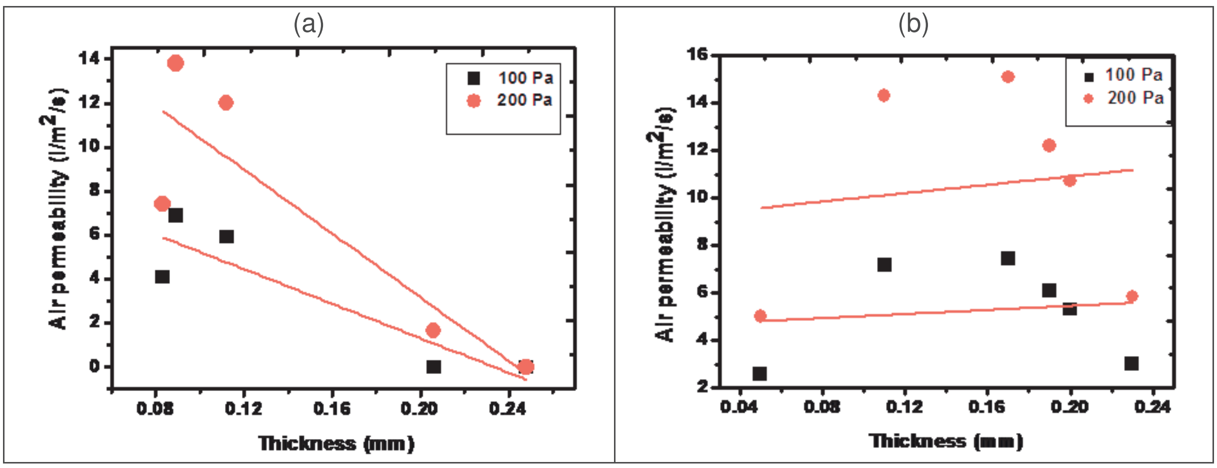


Figure 5 Air permeability of (a) Electrospun PUR nanofibrous layer embedded with silica aerogel) 100 & 200 Pa. and (b) Electrospun PVDF nanofibrous layer embedded with silica aerogel) 100 & 200 Pa

Lower air permeability causes lower air flow; consequently, more thermal insulation. The air permeability of electrospun nanofibrous layers are shown in the **Figure 5**. According to the figures; samples containing PUR nanofiber with double layer showed less air permeability. This behaviour can be attributed to the finer diameter of PUR nanofiber compared to PVDF nanofiber diameter. By increasing the number of nanofibrous layers, lower air permeability was achieved, confirming the relation of this important parameter with thermal insulation ability. The **Figure 5** shows that sample PUR4, PUR5 and PVDF5 were impermeable at 100 and 200 Pa. The experimental data of tested PUR and PVDF samples were found to be significant.

4. CONCLUSION

Literature searches on the subject of nanofibrous layers in thermal insulation reveal limited work using polymer nanofibers for thermal insulation applications. The effects of electrospun PUR and PVDF nanofibrous layers embedded with silica aerogel on thermal behaviour were studied. The results show enhancement in thermal insulation by increasing the number and the weight per unit area of both nanofibrous layers. Higher thermal resistance was observed in the case of samples containing PUR and PVDF nanofibrous layers, which can be attributed to the low air permeability and fiber diameter. Moreover, thermal measurements show that embedding silica aerogel in nanofibrous layers leads increased thermal insulation. Furthermore, weight and thickness can be reduced by means of nanofiber layers. The work presented in this paper did not show nanofibers to be useful for high loft thermal insulation. However, they may be useful as components in hybrid battings with high bulk densities. Fibers below 1 μm in diameter are not thermally efficient at low fiber volume fractions; this corresponds with previous research on fiberglass insulation. Performance gains in existing thermal insulation materials may be possible by incorporating a proportion of nanofibers into the structure, but large diameter fibers would still be necessary for durability and compression recovery. Although the electrospun nanofibrous layers have been proposed to strengthen the aerogel, the preparation technique of the electrospun nanofibrous layers embedded with aerogel with larger size, and lower thermal conductivity has to be further developed.

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