

APPLICATION OF NANOFIBER TECHNOLOGY TO NONWOVEN THERMAL INSULATION

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ABSTRACT

Nanofiber technology (fiber diameter less than 1 micrometer) is under development for future Army lightweight protective clothing systems. Nanofiber applications for ballistic and chemical/biological protection are being actively investigated, but the thermal properties of nanofibers and their potential protection against cold environments are relatively unknown. Previous studies have shown that radiative heat transfer in fibrous battings is minimized at fiber diameters between 5 and 10 micrometers. However, the radiative heat transfer mechanism of extremely small diameter fibers of less than 1 micrometer diameter is not well known. Previous studies were limited to glass fibers, which have a unique set of thermal radiation properties governed by the thermal emissivity properties of glass. We are investigating the thermal transfer properties of high loft nanofiber battings composed of carbon fiber and various polymeric fibers such as polyacrylonitrile, nylon, and polyurethane. Thermal insulation battings incorporating nanofibers could decrease the weight and bulk of current thermal protective clothing, and increase mobility for soldiers in the battlefield.

1. INTRODUCTION

We are addressing the mechanisms of heat transfer through fibrous insulation where the fiber diameter is less than 1 micrometer (μm). The thermal insulating efficiency of fiber-based insulation is known to increase as the fiber size is reduced. Recent advances in the technology of producing nanofibers have revealed a gap in our knowledge about the heat transfer behavior of low-density nanofibrous layers. Radiative transfer through beds of fibers where the fiber diameter is much less than infrared wavelengths is not well understood, either theoretically or experimentally. 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.

Note: *Nanofibers* are generally defined in the U.S. textile industry and Japanese and Korean strategic research initiatives as fibers of less than 1 μm in size. This is in contrast to the National Science Foundation current definition of *nanotechnology*, where structures are less than 0.1 μm in some critical dimension.

Convective heat transfer (heat carried by gas flow) through nanofiber beds is qualitatively different when fiber diameters begin to approach the mean free path of air molecules ($\approx 100\text{nm}$). We are investigating models and experimental verification of the influence of slip flow on convective heat transfer in nanofiber beds. However, radiation heat transfer is the most challenging aspect of this problem. There are deficiencies in the classical approaches to treating thermal radiative transfer through nanofibrous layers, especially when the fibers are composed of polymers, conductive materials (such as carbon), or contain nanoparticulate fillers that act as infrared absorbers or emitters. The greatest challenge in this work is to reconcile radiation models with experimental measurements of heat transfer through nanofiber insulation materials.

2. APPROACH

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 (the 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 analyze both radiation heat transfer and convection heat transfer mechanisms.

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1.1 Radiation Heat Transfer

Research on glass fiber insulation circa 1940-1960 suggests that fiber diameters in the range of 5-10 μm possess the best thermal barrier properties (Fig 1). Infrared radiation (heat) wavelengths are in the range of 0.7 to 100 μm , suggesting those fiber diameters less than 0.5 μm would be too small to interact with thermal radiation. However, it is known from later studies that fibers smaller than 1 to 3 μm can increase the thermal resistance of polymer fiber insulation materials (as evidenced by commercial microfiber insulation materials such as Thinsulate® and Primaloft®). Experimental data for fibers less than 5 μm is sparse, incomplete, and sometimes contradictory. Fig. 2 shows some contrasting data for glass fibers. It is evident that there are still benefits to decreasing the fiber size down to 2.5 μm even for fiberglass.

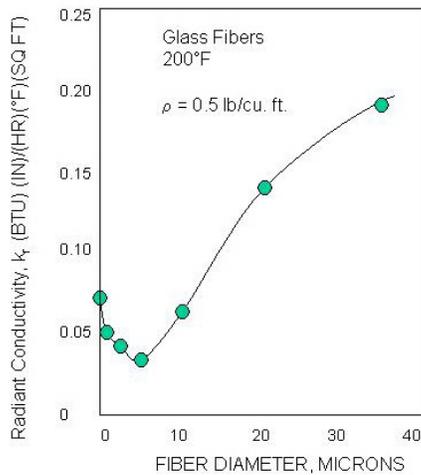


Fig. 1. Optimum glass fiber size for minimum thermal radiation is about 5 μm (Larkin and Churchill, 1959).

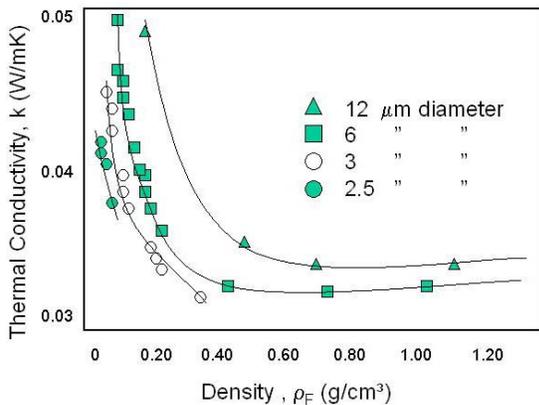


Fig. 2. Contrasting data shows thermal conductivity is still decreasing below 5 μm fiber diameter (Dent et al., 1984).

The importance of the radiation component in heat transfer through fibrous insulation increases with temperature, and is important even at the relatively low temperatures experienced in clothing applications. Thermal radiation can account for 40 to 50% of the total heat transfer in low-density fibrous insulation at moderate temperatures. Modeling techniques account for radiative transfer by assuming that the fibers absorb, emit, and scatter thermal radiation (McKay et al, 1984; Hager and Steer, 1967; Davis and Birkebak, 1973; Lee and Cunnington, 1998, 2000). Many of the simplest models in the past assumed that the fibers only absorb or emit infrared, but this can lead to significant errors (McKay et al, 1984). The electromagnetic/optical properties of fibers have been found to be very important in radiative transfer (optical includes infrared wavelengths). The scattering and absorption parameters of fibrous insulation materials depend on the optical properties of the polymeric material, as well as the size, shape, and orientation of the fibers. For glass fibers, the standard assumption is that glass does not absorb the thermal radiation, and there is little interaction between radiation and other modes of heat transfer, unlike strong absorbers like most polymers. Predictions from a particular model (McKay et al., 1984), (Fig. 3) show an example for polyester fibers where the optimum diameter is around 1 μm , but changes to the dielectric constant result in further increases in thermal efficiency for smaller fibers (conducting fibers reduce radiation heat transfer). A material such as meltblown pitch carbon fiber should also show this effect, because the fiber is conductive, colored black, and is a strong absorber and emitter of infrared. Another example is that the reflective coatings on silica fibers used for high-temperature applications (where thermal radiation is dominant) have been shown to reduce radiative heat transfer (Hass et al., 1997).

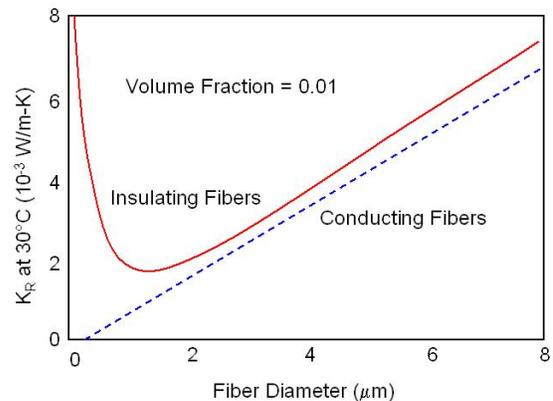


Figure 3. Predicted radiative conductivity as function of fiber diameter (McKay et al., 1984).

1.2 Convective Heat Transfer

The other major mode of heat transfer influenced by the submicron fiber size parameter is convective heat transfer. Convection may be natural (driven by heated air rising through the material), or it may be forced, driven by external pressure gradients, such as external wind, or motion of the body. Very fine fibers tend to damp out all convection because of their huge surface area, which impedes the free flow of air past the fibers. Theoretical relationships between gas permeability and fiber size for various volume fractions of fiber are useful in predicting the convective flow through fiber beds. Fig. 4 shows this type of correlation for beds of fibers greater than 1 micron in size, where air flow at different pressure gradients, humidities, and compression levels is used to characterize the mean fiber diameter (Gibson et al., 1999).

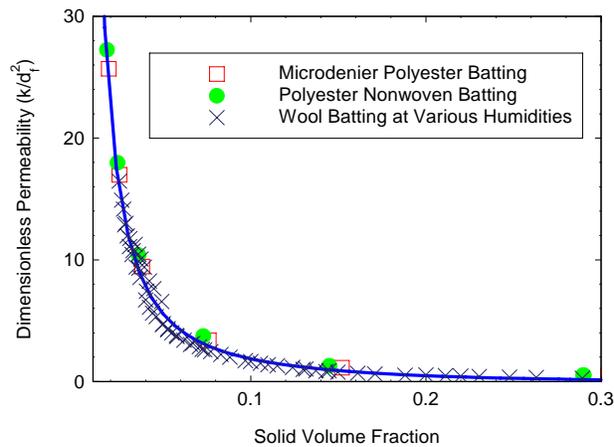


Fig. 4. Permeability correlation for three fibrous nonwovens. k on the y-axis is gas permeability coefficient, and d_f is fiber diameter.

This measurement/correlation technique provides the important properties required for predicting the onset of natural convection, and the influence of forced convection due to external pressure gradients. However, for the nanofibrous beds, additional modeling is required to account for the gas slip at the fiber surface. When the mean free path of gas molecules ($>0.1 \mu\text{m}$) becomes comparable to the fiber diameter, there is gas slip at the fiber surface, and more gas can flow through the fiber mass than would be expected based on continuum flow assumptions. This is the same reason that nanofiber filters are unexpectedly effective, since a higher air flow rate can be achieved at a lower pressure loss than would be expected based on a classical correlation as given in Fig. 4. It is possible that the onset of natural

convection for nanofiber battings occurs at an earlier point than is expected based on continuum assumptions. Some of the convective effects could be observed experimentally when heat flow measurements are compared between the “heat flow up” and “heat flow down” configurations in the thermal conductivity apparatus.

2. MATERIALS AND METHODS

Materials for experimental investigation and theoretical analysis are drawn from standard and developmental materials with a wide range of fiber properties and compositions. The materials include natural protein fibers (down and wool), commercial polyester high-loft insulations, meltblown pitch carbon fiber, electrospun polyacrylonitrile, and silica aerogel-impregnated flexible fibrous insulation. Examples of a few of the fibrous insulation materials examined in this study are shown in Fig. 5 and 6.

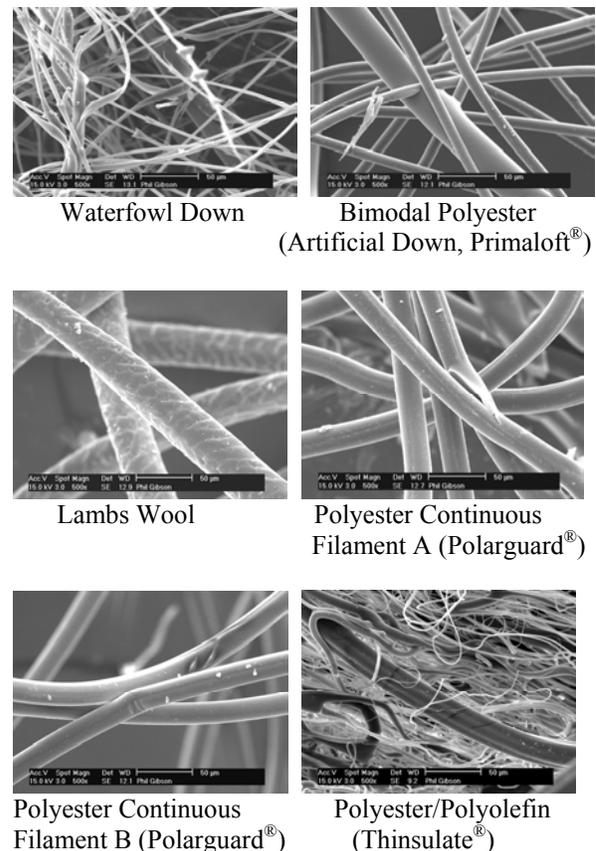


Fig 5. Comparative fiber sizes of various fibrous thermal insulation materials (500x).

Nanofiber insulation materials were obtained in the form of electrospun polyacrylonitrile (PAN) from

Drexel University, and meltblown carbon pitch nanofiber battings were obtained from the University of Akron (Fig. 6).

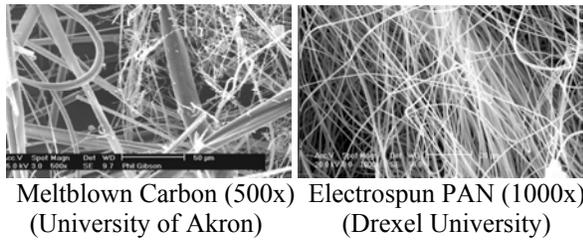


Fig 6. Nanofiber thermal insulation materials.

The PAN nanofiber battings were produced in various configurations and fiber diameters, but the most useful samples proved to be a set of three variations: 1) “Small” nanofiber battings (mean diameter of 0.44 μm); 2) “Large” nanofiber battings (mean diameter of 1.0 μm); and 3) “Mixed” nanofiber battings (blend of “Large” and “Small” fibers).

Partial carbonization of a duplicate set of these PAN samples permit the direct comparison of the importance of fiber optical properties to radiant heat transfer in low density battings (white versus black fibers). The meltblown pitch carbon nanofibers from University of Akron provided a useful comparison with another set of carbon fibers with different properties

Shown in Fig. 7 is a high-performance benchmark comparison material, the fiber/aerogel composite. Aerogel is an open cell transparent material, usually composed of silica, in which 90% of the pores range from 10 to 50 nm. Fiber-supported flexible aerogels have polymer or carbon fibers dispersed in an aerogel matrix. Silica aerogels are transparent to thermal radiation, and do not perform well as insulation alone. However, the fiber/aerogel composite becomes an effective insulator since the aerogel matrix suppresses conduction and convection, and the fibers reduce radiation heat transfer while increasing the strength of the brittle and weak aerogel matrix (Lee and Cunningham, 2000). Although the aerogel/fiber composites have good thermal properties, they paradoxically carry a weight penalty since 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 low bulk densities as fibrous insulation, but they do achieve better thermal resistance for an equivalent thickness of material.

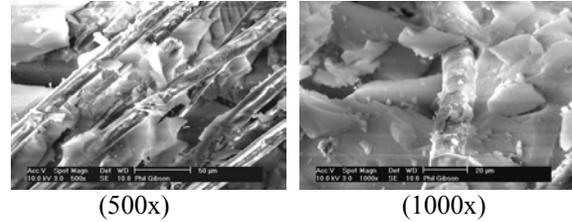


Fig. 7. Flexible aerogel insulation showing aerogel matrix around polyester fibers (1000x).

To investigate the comparative thermal properties of insulating materials, ASTM C-518 “Standard Test Method for Steady-State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus” is used (Lee, 1984; Gibson, 1990). Typical test conditions are 50°C on the upper plate, and 10°C on the lower plate. Testing in the heat flow down configuration minimizes convective heat transfer through the porous insulation materials, so that the primary heat transfer mechanisms are solid/gas conduction, and thermal radiation. A schematic of the test system is shown in Figure 8. The lower plate assembly is movable so that the insulation test sample may be tested at various thickness and compression levels.

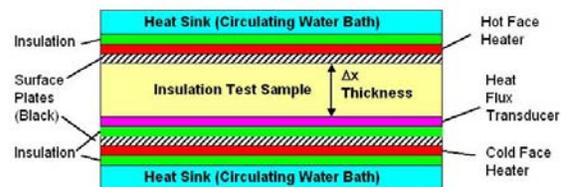


Fig 8. Heat flow meter schematic for thermal insulation testing. Thermocouples for temperature measurement at plate and heater surfaces not shown.

3. RESULTS

Thermal conductivity as a function of compression for several of the insulation materials pictured in Fig. 5 is shown in Fig. 9. Of particular interest are the results for the two nanofiber insulation materials (electrospun polyacrylonitrile and meltblown pitch). Both materials show excellent reduction in overall heat transfer compared to standard low-density fibrous insulating materials (at bulk densities below 50 kg/m^3). The meltblown pitch carbon nanofiber battings, in particular, show some interesting unexplained behavior by showing superior insulation at low bulk density values, then becoming more conductive than would be expected at high compression levels.

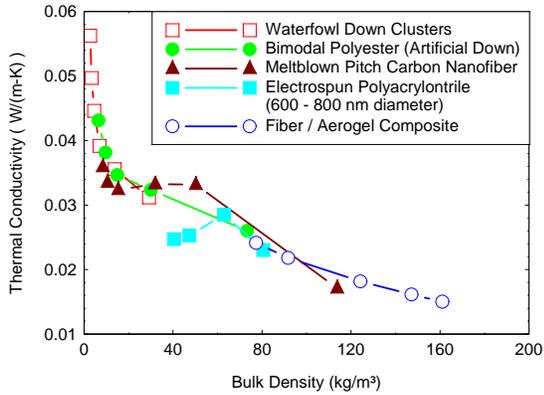


Fig. 9. Thermal conductivity measurements as a function of density for battings of various fiber types and sizes.

Thermal conductivity testing confirmed that decreasing fiber diameter tends to increase the thermal resistance of fibrous insulation materials. Fig. 10 shows that the effect is most pronounced at low bulk densities and high porosity, where there is a large separation between fibers, and where thermal radiation is the dominant mode of heat transfer. At high compression levels, the advantage of small fiber diameters becomes much less important.

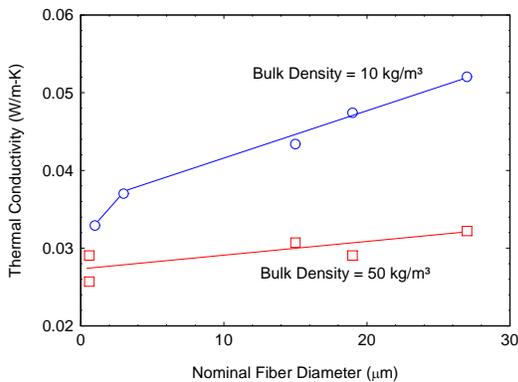


Fig. 10. Effect of fiber diameter on thermal conductivity at two compression levels for fibrous insulation materials.

An important real-world feature for insulating materials used in military clothing and sleeping bags is the weight, since soldiers must often carry their cold weather clothing and sleeping bags, along with all their other gear. Insulating weight efficiency in terms of thermal resistance ($m^2\cdot K/watt$ or RSI) per unit areal density is one useful comparison between materials. Fig. 11 shows that waterfowl down, by virtue of its high loft and low weight, is an excellent insulator on this basis, providing superior insulating power for a given area, especially at large thicknesses. In this application, we see contrasting trends for the two

nanofiber insulations – the meltblown pitch compares well with the down clusters, while the electrospun polyacrylonitrile (PAN) suffers a weight penalty. The physical arrangement of the fibers influences this comparison since the electrospun PAN fibers have no large fibers to support loft -- the electrospun fiber bed was fabricated in thin low-porosity layers. The carbon pitch nanofibers include a large distribution of fiber sizes, and the large fibers help support the structure, resulting in a much thicker and “fluffier” fiber bed, which is more comparable to waterfowl down.

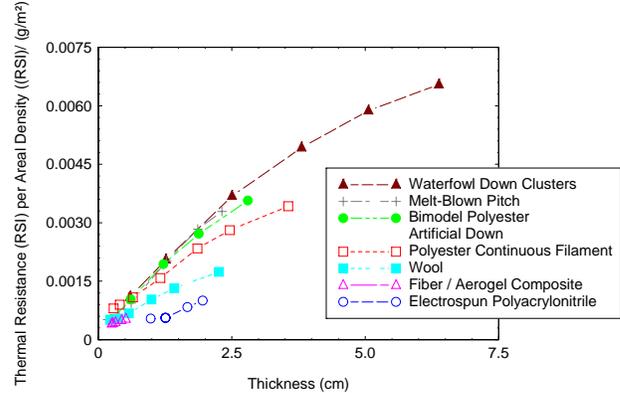


Figure 11. Weight efficiency of various fibrous insulation materials, including aerogel composites.

As mentioned previously, fiber/aerogel composites have been shown to have superior insulation properties for applications where thickness is of concern. Although they may suffer a weight penalty with respect to high porosity fibrous insulation materials, aerogel/fiber composites have excellent insulation per unit thickness properties, as shown in Figure 12. Nanofiber nonwovens might also be integrated into these types of materials, either directly in the matrix, or as discrete fibrous layers in series with the composite.

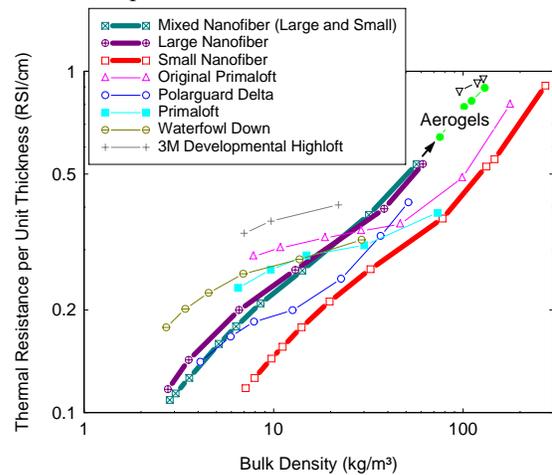


Fig. 12. Fiber/aerogel composite layers have superior insulating value per unit thickness.

In general, the thick high loft electrospun insulation materials did not show significant thermal performance improvements over commercially-available insulations. Fig. 13 shows that the pure nanofiber battings have poor insulation properties at low densities, and some gains when tested at high densities (compressed). However, both Figures 12 and 13 show that the compressed nanofiber insulation properties approach those of the aerogel/fiber composites at high bulk densities.

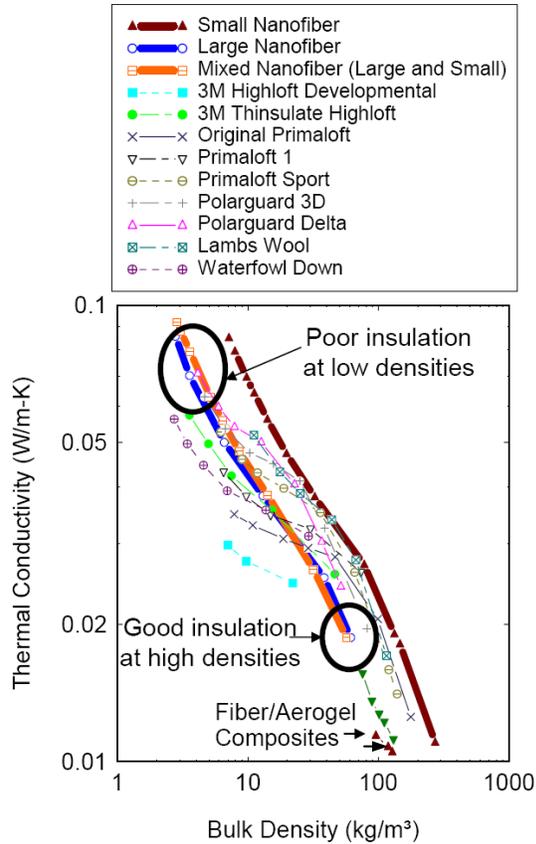


Fig. 13. PAN nanofiber battings show best thermal insulation performance at high densities.

Insulation materials composed solely of electrospun nanofibers lack resiliency for practical applications, as shown in Fig. 14. Assemblies of these fibers are stable only at high bulk densities, and are extremely susceptible to collapse due to liquid capillary forces or physical compression. Insulation materials incorporating small diameter reinforcing fibers must include a significant portion of larger diameter reinforcing fibers to enable recovery of loft after compression (Dent et al., 1984).

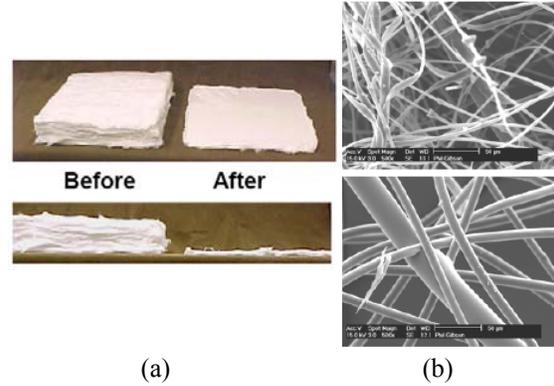


Fig. 14. (a) Thickness loss of PAN nanofiber battings after thermal conductivity testing under compression; (b) Inclusion of large diameter reinforcing fibers aids loft recovery after compression (down and polyester)

Different fibrous materials may be combined together to enhance the thermal insulation properties of a composite insulation. This technique of layering is also a useful way to investigate the influence of thermal radiation heat transfer through thin fibrous layers. The heat flow meter apparatus is designed for thick materials, and is not optimal for investigating heat transfer in thin materials (materials less than 1 cm thickness). The intrinsic insulating properties of thin materials such as electrospun nonwovens and the aerogel/fiber composites, maybe be tested in series with a thick nonwoven insulation material,

An example of this technique is shown in Fig. 15 for a thin layer of electrospun PAN placed between two much thicker polyester insulation layers. Fig. 15 shows the arrangement of the test samples in the heat flow meter and the measured thermal resistance of the two cases: 1) the two polyester batting insulation layers alone, and 2) the two polyester batting insulation layers with the PAN electrospun layer in the middle.

The influence of the nanofiber layer is negligible at high total composite thickness, but slightly increases total thermal resistance at lower composite thickness, where the electrospun PAN fiber layer is a larger percentage of the thickness of the composite. Because of the “precompressed” nature of the electrospun PAN fiber layer, it is probably not changing thickness to an appreciable extent; the polyester batting layers are being compressed on either side of the PAN layer.

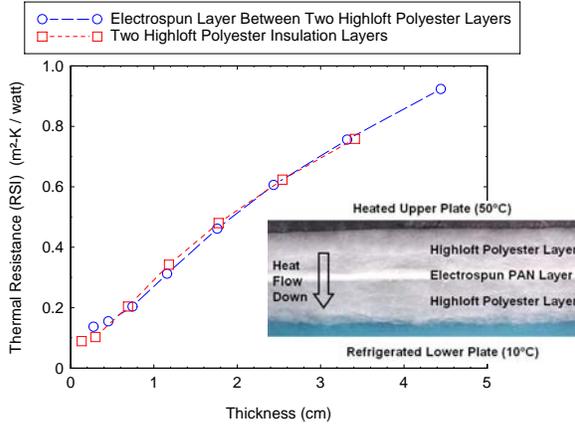


Fig. 15. Effect of a single thin nanofiber layer in between two high-loft insulating layers.

3.1 Pyrolysis of PAN Nanofiber Battings

Polyacrylonitrile is a well-known precursor used in the preparation of high-strength carbon fiber. The first stage in producing carbon fiber is to partially oxidize the PAN fibers in the presence of oxygen, prior to the final carbonization step, which is carried out in an inert atmosphere at high temperatures. The preliminary partial pyrolysis step has been shown to produce a fibrous insulation material that is useful in its own right, due to its thermal stability and inherent fire-retardancy (Bourbigot and Flambard, 2002). This initial pyrolysis step was carried out for the electrospun PAN nanofiber battings to obtain a direct comparison between battings that are similar in fiber diameters and structural parameters, but differed significantly in infrared radiative properties. Fig. 16 shows a typical sequence in the process of pyrolyzing the electrospun nanofiber battings.



Fig. 16. Polyacrylonitrile (PAN) nanofiber battings partially oxidized in the presence of oxygen in the range of 170°C – 220°C.

To date, only the “Small” (less than 500 nm)” electrospun nanofiber samples have been partially pyrolyzed. Fig. 17 shows that the thermal conductivity of the pyrolyzed PAN nanofiber sample was reduced significantly. Pyrolysis of the “Large” ($\approx 1 \mu\text{m}$) and the “Mixed” nanofiber battings has yet to be carried out, and it will be interesting to see if the properties of those materials show similar improvements.

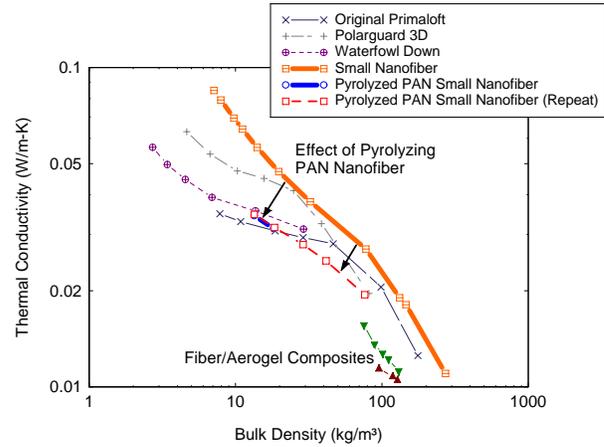


Fig. 17. Pyrolyzed PAN nanofiber insulation showed significant reduction in thermal conductivity.

3.2 Meltblown Pitch Nanofiber Battings

Initial thermal conductivity testing of meltblown pitch carbon nanofiber samples was promising (Fig. 9). The initial sample incorporated many fibers less than $1 \mu\text{m}$, but also included a large proportion of larger diameter fibers that produced improved compression properties as compared to the electrospun PAN nanofiber battings. However, problems with the production apparatus produced later samples that were matted, clumped, and generally unsuitable for testing of material properties. A carding technique was employed to generate dispersed nanofibers that could then be combined with an existing continuous filament polyester batting (Polarguard®). This produced a composite structure that incorporated nanofibers, but relied on the larger diameter polyester fibers to support the nanofibers and provide better compression recovery for the composite samples.

Fig. 18 shows that a 10% by weight add-on level of carbon nanofibers resulted in an increase in thermal insulating efficiency of the continuous filament polyester insulation. Further iterations on blended nanofiber/macrofiber composites are planned to fully explore this trend.

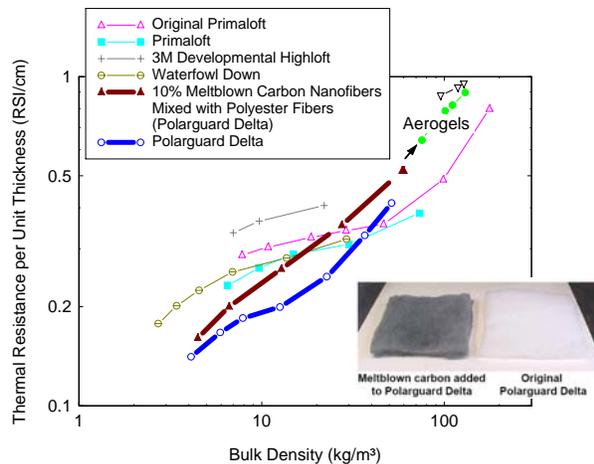


Fig. 18. Meltblown pitch carbon nanofibers blended into continuous filament polyester batting showed an improvement in thermal insulation properties for the composite structure.

CONCLUSIONS

Literature searches on the subject of submicron fibers in thermal insulation reveal no fundamental or applied work using polymer nanofibers for thermal insulation applications. Nanofiber research and technology has focused on filtration applications, chemical/biological protection, and biomedical applications. This research has exploited the high surface area and small pore size of nanofiber membranes and nonwovens, mostly in thin sheet form (Huang, et al, 2003a, 2003b).

The work presented in this paper did not show nanofibers to be useful for highloft 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. Modification of fiber infrared radiation properties may also improve the thermal insulating efficiency of nanofiber layers.

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