Nanoengineering of Sol-Gel Materials for Thermal Insulation

Kiran Gollakota
kgollakota@lawrenceville.org

Giulia Pantalone
gbpantalone@optonline.net

Kelsey Tripp
katripp@comcast.net

Wil Waters
rapidwaters1@msn.com

1 Abstract

In this study, novel sol-gel materials with low thermal conductivities were synthesized for the purpose of creating a material that would improve the insulating capacity of a commercial down vest. Seven types of fibers were used to create composite gels in Ludox™ suspensions, with each gel containing one type of fiber. The thermal conductivities of the twenty-four fiber-gel composites were then tested using a hot water bath to create temperature differences. It was found that the suspension containing a matrix of silicon carbide polymer fibers provided the best thermal insulation for the purposes of this investigation, increasing upon the insulating capacity of a manufactured down vest by 7.7%.

2 Introduction

The development of nanotechnology has opened many new doors in the field of materials science and engineering. It has enabled researchers to manipulate and fabricate materials at the nanometer scale, allowing them to improve upon the properties of a variety of materials. In particular, the sol-gel process, which is a method of fabricating solid materials from a chemical suspension, has benefited greatly from the emergence of nanotechnology. For example, the sol-gel process can be used to improve insulation in certain materials.

Current methods of insulation in clothing include the use of down feathers and synthetic foams. Although down is one of the most efficient insulators on the market, it is expensive and difficult to obtain. In the past, researchers have attempted to emulate the insulating quality of down by producing synthetic materials such as Thinsulate™. However, these materials are not as effective as natural down feathers: down is about three times warmer per ounce than the best synthetic insulation available.[1]

It is natural for the sol-gel process to be applied to the manufacturing of insulating materials. The versatility of the process, as well as the relative ease with which composites can be created, makes it an ideal method to support and improve current systems of thermal insulation. Moreover, the sol-gel process is easily translated from the lab to the factory for two main reasons:

- The process does not require a complete redesign of current insulating methods: the gels can be applied on top of – rather than in place of – commonly used natural and synthetic insulating materials such as down and polyester.
- The process is relatively inexpensive and does not require a great deal of advanced infrastructure to carry out.

Thus, using the sol-gel process to improve current standards of thermal insulation in clothing is both practical and useful.

To that end, twenty-four composite gels were created in a laboratory environment. Each gel contained a single type of fiber in a Ludox™ sol suspension, and the thermal conductivities of the gels were tested.

While this body of work represents only one of the first steps in the application of sol-gel to the field of thermal insulation, the process has great potential to contribute to the science of insulating materials.

3 Background

There are two main methods to produce sol-gels. One method uses alkoxide solutions as a precursor for the gel, while the other uses a colloidal sol as a precursor. Colloidal sols provide a time advantage, in that they dry more quickly than sols made with alkoxides, which take over a month to fully dry.

Colloidal sols, the type of sol used in this experiment, contain solid nanoparticles in a liquid suspension. Commercially available pre-mixed sols such as Ludox™ form a gel when the particles aggregate. Aggregation can be induced by changing the pH or concentration of the sol. As the sol-gel dries, the linked particles form a single, networked supermolecule that contains nanosized pores. [2]

Porosity is an important factor in determining the insulating properties of solid materials. Pores allow a solid to trap air, which increases its insulating capacity because, compared to other insulators, air has an extremely low thermal conductivity. [3], [4] In fact, the presence of pores in solids can reduce thermal conduction by a factor of 500, as compared to nonporous solids. [5]

In addition to porosity, other factors contribute to a material's ability to contain heat. By adding secondary materials to the gel to form a composite, one can take advantage of both the porous, continuous network of the sol, and the additional insulating properties of the additives. At the beginning of the gelling process, polymer fibers can be added to the sol. Once the gel dries, the polymers become integrated into the composite's skeletal network. The concentration, orientation, and distribution of polymer fibers within the network will add additional properties to the composite. Polymers arranged in a uniform and continuous pattern give the material greater strength in a given direction. Randomly oriented and discontinuous fibers allow the composite to have multi-directional strength under isotropic stresses. The randomly interlocking distribution of polymer fibers can also have an insulating effect by trapping air, which is especially true when using porous polymers such as polypropylene fibers.[6]

Natural goose down feathers in manufactured products such as pillows and jackets provide such great insulating capacity due to the similar random arrangement of the feathers: each tiny feather has hundreds of interlocking filaments that form an insulating network that traps a layer of air within the material. [1]

4 Related Work

Since the sol-gel process is a relatively new technology, novel applications are constantly being developed. Researchers have explored many useful techniques in order improve different materials through the sol-gel process. Dr. Lisa Klein, currently a professor at Rutgers University, performed much of the early work regarding the sol-gel process.[2] Her research showed that colloidal sols take only a few days to gel, have larger interconnected pores, and crack much less easily. She also discovered that alkoxide gels exhibit a much smaller pore structure, but they take over a month to dry and crack easily.

In another paper, Dr. Klein suggests that the sol-gel process could be used as a form of insulation.[7] Aerogels, a form of sol-gels, are said to be "super insulators", and her research displays the potential for many applications of aerogels. Some of these uses include insulation for greenhouses, solar energy, and walls. Aerogels were not used in this research, but they provided the inspiration for the implementation of sol-gel as insulation in jackets. The sol-gel process described in Dr. Klein's work is ideal for insulation because sol-gel can be formed in a thin film—suitable for deposition on a fabric—and the pores in the sol-gel trap air and create excellent insulation.

In recent years, the sol-gel process has been used to improve textiles' qualities, such as their durability.[8] In Mahltig's research, silica sols were found to provide protection for the textile against corrosion from water, oil and soil. Another research project involving the sol-gel process explored how to improve the cleaning properties of textiles.[9] TiO_2 and SiO_2 sol-gels were coated on cotton fabrics, and then tested with Neolan Blue 2G Dye. The resulting material showed much potential of sol gels for the development of self-cleaning fabrics.

Given the many breakthroughs that have been made utilizing the sol-gel process in improving textiles, it is logical to test sol-gels for other implementations. A logical application would be to use sol-gels as an insulation to improve down jackets. Research has shown that sol-gels have favorable insulating properties, in addition to their other useful characteristics.

5 Experimental

To establish a standard to which the synthetic sol-gel materials could be compared, the thermal conductivity of a commercially available nylon vest was measured.

A 225 cm^2 swatch of the vest was secured to a mercury thermometer such that the vest completely covered the bulb of the instrument. The thermometer and vest were then placed in an empty plastic bag, and the bag was submerged in a beaker containing water heated to 40 °C. The time it took for the covered thermometer to register a 10 °C increase in temperature was measured.

The fiber-composite gels were then created using the sol-gel process.

Ludox™ was obtained and used as the sol, while an aqueous sodium chloride solution was used as the gelling agent. Three sets of samples were prepared: one made with 0.5 M sodium chloride solution, one made with 1.0 M sodium chloride solution, and one made with 1.5 M sodium chloride solution. Each set contained eight gels.

Seven of eight gels in each set were fiber-gel composites; one was a control sample to which no fibers were added. No gel contained more than one type of fiber. The fibers used were: gold-colored, hollow polypropylene fiber; white PVC fiber; black nylon fiber; clear , porous polypropylene fiber; silicon carbide fiber; white polypropylene string; and white polypropylene straws.

The fiber-gel composites were created by mixing the fibers into 20 mL of sol prior to the addition of a further 10 mL of salt solution. It was critical that the fibers were added prior to the addition of the salt solution, as this ensured that no gellation could occur before the fibers were added.

The twenty-four gels were then allowed to dry for a period of forty-eight hours. Thermal conductivity tests were then performed on each gel. Each conductivity test was performed in a manner similar to that used for the initial standardization test, with some notable exceptions:

- Rather than wrapping the thermometer in the sample, the instrument simply rested upon it. This change was necessitated by the relative rigidity of the samples, which diminished their ability to completely cover the bulb of the instrument.
- The sample was contained in a petri dish rather than a plastic bag. It was placed directly on a support that was submerged just under the waterline of the hot water bath.
- The time for the thermometer to register a 5 °C change, rather than a 10 °C change, was measured. A change of 5 °C was tested instead of 10 °C because there was only a short period of time in which the samples could be tested, and it was necessary to test all of them on the same day to maintain consistency.

The gel with the least thermal conductivity – that is to say, the gel that was the best thermal insulator – was determined through this conductivity testing.

Results from the conductivity testing showed the silicon carbide gel to be the most effective thermal insulator, the silicon carbide composite was then implemented on the vest.

A new set of silicon carbide composite gels was created for implementation on the vest. After being allowed to gel for approximately five minutes, the material was applied to the inner lining of the vest, between the fabric and polymer filling. A thermal conductivity test was then performed on a swatch of material from the sol-gel vest in a manner identical to that used for the initial standardization test.

6 Results and Discussion

Each of the twenty-four samples had properties that differed depending upon its molarity and the polymers that it contained. For the purposes of this experiment, the gels were evaluated on the following criteria:

- Fastest time-to-gel, while still maintaining structural integrity: A desirable gel should be synthesized quickly but gel and dry uniformly.
- Fiber aggregation: The polymer fibers should be integrated into the sol-gel network, be distributed evenly throughout the gel, and be neutral in charge, to ensure that they will not be attracted to the material being coated in the gel.
- Drying pattern: Once dried, the gel should have as few cracks as possible, and appear as a single smooth layer.
- Thermal conductivity: The gel should have a low rate of thermal conduction, based upon the heat bath test.

Time-to-Gel:

The time-to-gel was determined by the molarity of the sodium chloride solution added to the sol. The gelling times elapsed as expected; the 0.5 molar solutions had the longest time-to-gel and the 1.5 molar solutions had the shortest gelling time. However, the 1.5 M solution induced gelling too quickly, creating an inhomogeneous gel (Figure 5a). Almost immediately upon the addition of the solution, the sample began to solidify and could not be mixed properly. The 0.5 M solution had a time-to-gel of several hours, while the 1.0 M solution took several minutes to gel.

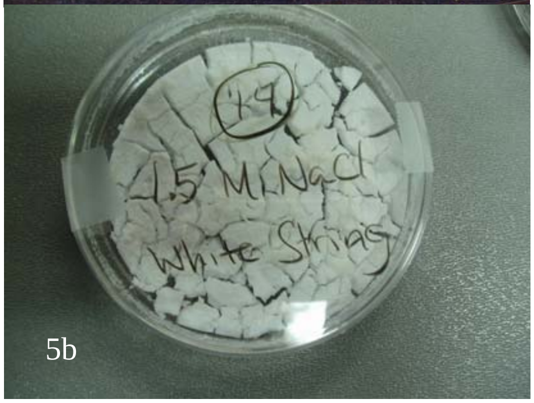

Figure 5a A 1.5 M gel sample with polypropylene fibers, just after the addition of the gelling agent.
Figure 5b A completely dried 1.5 M gel sample with polypropylene string fibers.

Fiber Aggregation:

The substances added to the Ludox™ were carefully selected. The gold polypropylene fibers and white polypropylene straws were hollow and therefore likely to trap extra air inside the gel. The other polypropylene fibers and black silicon carbide string were also chosen for their insulating properties.

The black nylon fibers, gold polypropylene fibers, and polypropylene straws remained floating on the surface of the gel and did not distribute throughout the surface area evenly. These fibers are nonporous, and compared to the porous fibers, did not absorb gel and sink. The straws exhibited a slight charge and were attracted to the sides of the dish

The silicon carbide fiber and the polypropylene string were the most

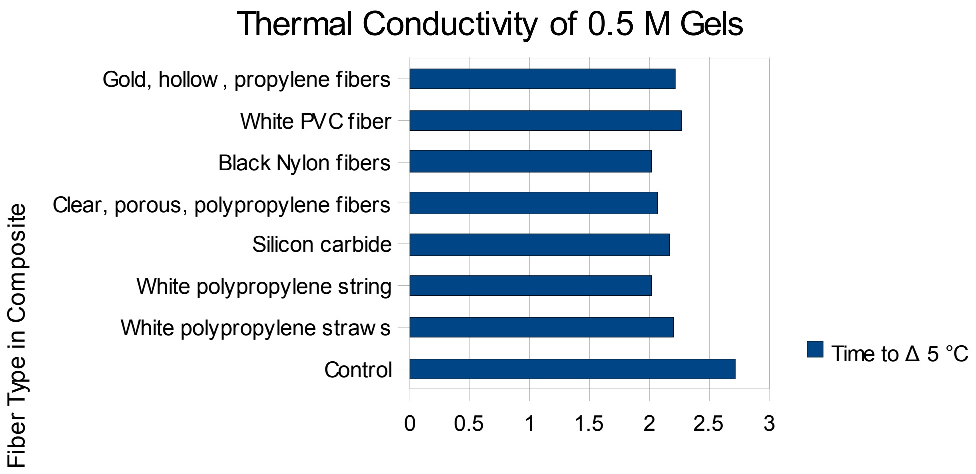

Figure 1 The relative thermal conductivities of each of eight 0.5 M gel samples, measured by the time taken to register a five-degree change in temperature.

Time to Δ 5 °C (min)
Figure 1

absorbent and distributed relatively evenly throughout the gel. These samples also remained more intact than the others did when dried because the polymers were integrated into the gel network.

Drying Pattern:

After 48 hours, all of the samples had dried. Every sample had experienced cracking, warping, and shrinkage. The degree to which each sample experienced these defects was correlated to the concentration of the gel. The 1.5 M gels were the most cracked because they had gelled too quickly and the material was not uniform (Figure 5b). The 0.5 M and 1 M gels were less cracked and were more consistent throughout the gel (Figure 6). Gels whose fibers were smaller and more deeply embedded experienced less warping and shrinkage, as the fibers added strength to the gels and were able to prevent them from distorting.

Figure 6 The cracking pattern in a dried 0.5 M sol-gel sample.

Thermal Conductivity:

The thermal conductivities of the various fiber-gel composites were dependent upon both the concentration and the fibers that were added to the sol. In no two sets of molarities did the same composite have the greatest insulating capacity.

Figures 1, 2, and 3 present the results of the aforementioned thermal conductivity test of the 0.5 M, 1 M, and 1.5 M composite gels, respectively.

The 1.0 M silicon carbide composite gel outperformed every other gel by a considerable margin, as can be seen from the figures above. The silicon carbide gel performed well because of the fiber's naturally low thermal conductivity. Moreover, the 1.0 M gel had greater consistency across its surface area compared to the 0.5 M and 1.5 M

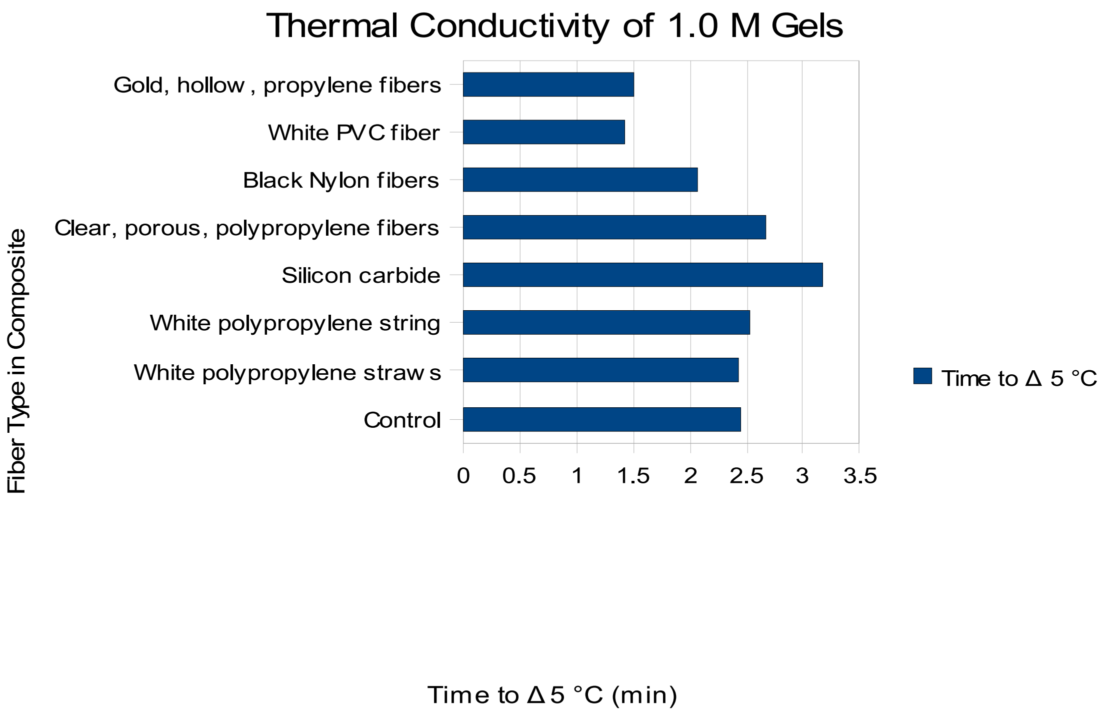

Figure 2

Figure 2 The relative thermal conductivities of each of eight 1.0 M gel samples, measured by the time taken to register a five-degree change in temperature.

Figure 3 The relative thermal conductivities of each of eight 1.5 M gel samples, measured by the time taken to register a five-degree change in temperature.

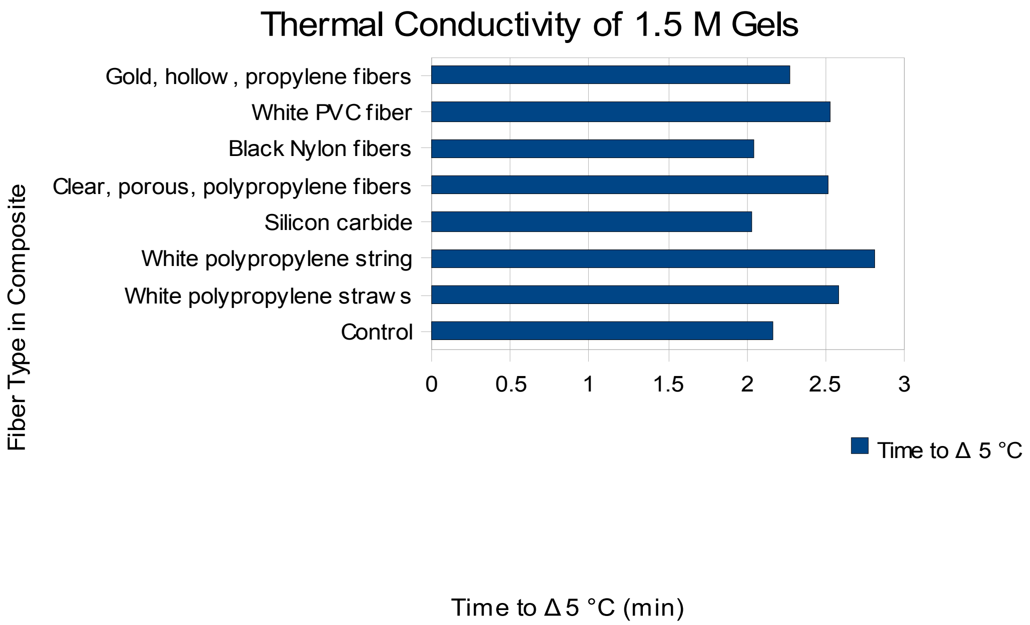

Figure 3

Figure 4 The relative thermal conductivities of each of six 1.0 M gel samples, measured by the time taken to register a ten-degree change in temperature.

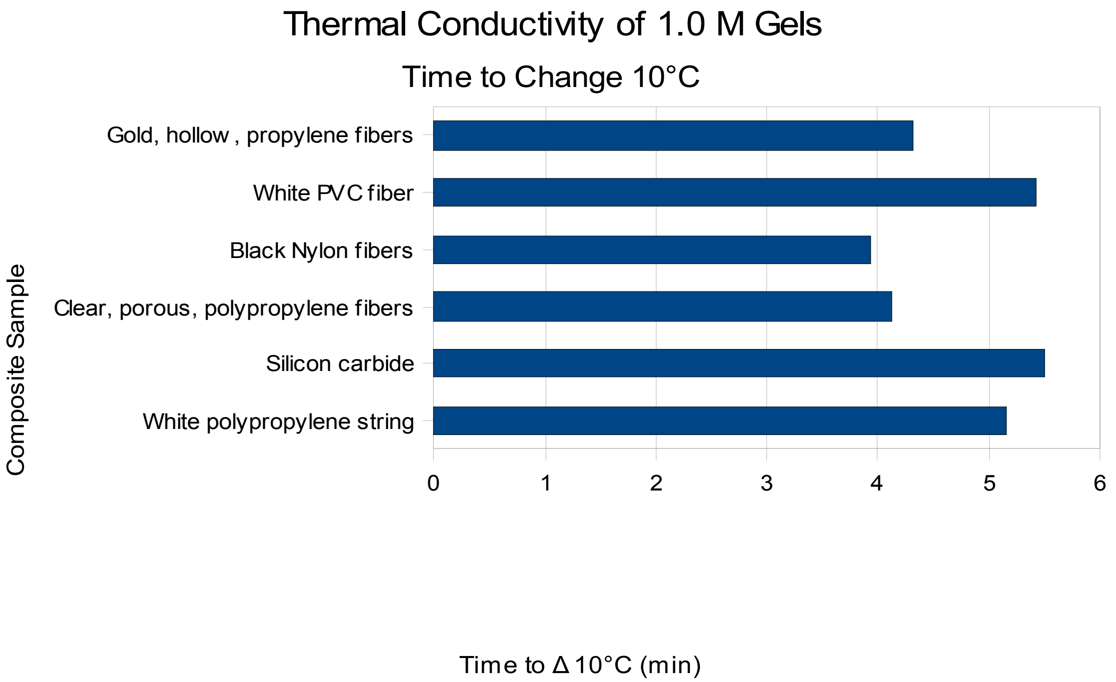

Figure 4

silicon carbide gels, which added to the composite gel's insulating capacity (Figure 7).

To confirm that these results could be replicated, six of the 1.0 M gel samples were retested in a hot water bath. The control gel and the polypropylene straw composite were not retested. Instead of only measuring the time taken to register a 5 °C change, a 10 °C change was measured. This served to confirm that the carbide gel's insulation could be sustained over a larger temperature range. The results from this set of conductivity tests are displayed in Figure 4.

Figure 7 The dried 1.0 M gel with silicon carbide fibers, chosen as the ideal insulating material.

Overall, the 1.0 M silicon carbide sol-gel composite performed the best on the thermal conductivity tests and was consistent with the other criteria considered when selecting the best material for this study. After coating the vest materials in the silicon carbide composite, the vest was considerably warmer.

Compared to the thermal conduction of the regular vest, which took 13 minutes and 3 seconds to register a ten-degree change in temperature, the composite-coated vest took 14 minutes and 3 seconds for the temperature increase. Thus, the materials created in the study had an insulating capacity that was 7.7% better than the commercially available vest.

8 Future Work

The vest created did have a higher thermal resistance than the commercial vest, but the process used to fabricate the vest was not practical and did not produce a product that could be marketed to consumers. Since the thin film was spread on the vest manually using spatulas, it was not possible to create a perfect thin film devoid of imperfections and areas of thicker gel.

However, there are methods for depositing thin films on substrates, such as fabrics and wafers. These methods include dipping and spin-coating. In order to deposit a thin film on the surface of a fabric, it will be necessary to use the dipping method. Methods for depositing thin films are detailed in [7].

It is certainly possibly to produce these vests on a large scale because of the ease of deposition of thin films with the proper machinery. This process will be simple and cost effective because it can be done at room temperature and pressure.

9 Conclusion

In this study, the colloidal sol route was used throughout the sol-gel process due to time constraints. In the future, utilizing the alkoxide-solution route may prove to have better results due to the differences in porosity and formation between the two different sols. Alkoxides produce ceramics with truly nanosized pores that are much smaller than pores created by colloidal sols. The main limitation in alkoxide processing is the gel’s drying time, which may exceed one month in order for the gel to become fully dry.

The colloidal sol-gel process utilized, however, may be more easily carried out on a larger scale. The colloidal sol-gels themselves gel and dry quickly (within a few days), and are easily applied to fabrics. This process could be adopted in the industry and used for large-scale manufacturing.

The insulation of the vest created in this study was improved by the sol-gel film that was added to the inner lining, but the methods used to create the vest were not practical for manufacturing. For the production of a product like this, spreading the gel film on the fabric manually with a spatula is not realistic for manufacturing on a large scale—nor is it precise. The gel that dried on the fabric was too thick, even though it was spread as thinly as possible. A more practical method must be found for depositing a very thin film onto the fabric to make industrial production possible.

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