MRS Advances © 2017 Materials Research Society
DOI: 10.1557/adv.2017.325

Flexible Polyisocyanate Based Aerogels

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ABSTRACT

Highly flexible, durable aerogels with textile feel were developed at Aspen Aerogels Inc. by sol-gel chemistry and supercritical CO_2 solvent extraction. These polyisocyanate-based aerogels reinforced with battings showed little to no brittle fracture with repeated flexing. The crosslinker, the isocyanate content and functionality played an important role on properties such as thermal conductivity, durability and flexural modulus at ambient and cryogenic temperatures. The polyisocyanate aerogels crosslinked with polyamine showed thermal conductivities as low as 18 mW/m-K at ambient pressure and those crosslinked with polyol had low flexural modulus at cryogenic temperatures. Applications of these aerogels in aerospace and diving are presented.

EXPERIMENTAL

Preparation

Polyisocyanate aerogels were prepared at isocyanate indices over 100 and target densities of 0.04 - 0.10 g/cc. Isocyanate precursors with a functionality ranging from 2 to 3 were used in these preparations. The catalysts were chosen from triazine derivatives (*i.e.* Polycat 41), quaternary ammonium salts (*i.e.* DABCO TMR) and tertiary amines. Polyisocyanate aerogels prepared in the absence of another crosslinking reagent are identified as PI. PI-PU aerogels were prepared by crosslinking the isocyanates with polyamines and PI-PUT aerogels were additionally crosslinked with polyols.

The isocyanate precursors were dissolved in tetrahydrofuran or acetone and mixed at room temperature with the crosslinkers and catalysts for various amounts of time. The resulting sols were poured in molds over non-woven fibers and left to gel at ambient temperatures. Gelation occurred in 3 minutes to 1 hour. Aging of the fiber reinforced gels in the preparation solvent was carried out for 1-3 days at room temperature or at temperatures up to 45 ºC. The solvent was exchanged several times prior to extraction with supercritical CO_2.

Testing methods

Fourier Transform Infrared Attenuated total Reflectance (FTIR-ATR) spectroscopy analyses were performed on aerogels, without fiber reinforcement, using a Perkin Elmer Spectrum 100 FTIR over the 4000-600 cm-1 range.

Thermal conductivity measurements at ambient pressures and temperatures were performed on a FOX300 apparatus manufactured by LaserComp Inc. according to ASTM C518 standard, using a plate temperature difference of 25 ºC.

The flexural modulus was measured at ILC Dover using a TA Instruments Q800 Dynamic Mechanical Analyzer. Durability was assessed at ILC Dover by flexing the aerogel materials in a Flex tester, using a Thermal Micrometeoroid Garment "sock" inflated to a pressure of 10 kPa and subjected to 45° flexions/extensions for 100,000 cycles at a rate of 30 cycles per minute.

Dust scores were qualitatively assessed by Crye Associates after flexing and cutting the aerogel materials. Dust was measured at Aspen Aerogels as percent weight loss after tumbling the aerogels with three baseballs in a commercial drier unit for 3 hours.
Laundering was performed at the Navy Clothing and Textile Research Facility in Natick, MA using a Whirlpool Commercial Washer, 4 pounds of cloth ballast and bleach. The test samples were then tumble dried with the same cloth ballast in a Whirlpool Commercial Dryer for 30 minutes.

RESULTS AND DISCUSSION

FTIR-ATR Characterization

The polyisocyanate aerogels were compared by FTIR-ATR in Figure 1. Carbonyl stretches occurred at 1713 cm^{-1} in the PI, 1668 cm^{-1} in the PI-PU and 1725 cm^{-1} in the PI-PUT aerogel. The carbonyl peak at 1725 cm^{-1} was identified as non-hydrogen bonded urethane carbonyl [1, 2] and that at 1668 cm^{-1} as urea carbonyl [2]. The band at 1411 cm^{-1}, characteristic of the isocyanurate ring [3] was present in the PI spectrum, but also in PI-PU and PI-PUT spectra. As expected, the PI-PU and PI-PUT crosslinked with polyamine showed the NH stretching at around 3300 cm^{-1} indicative of urea formation.

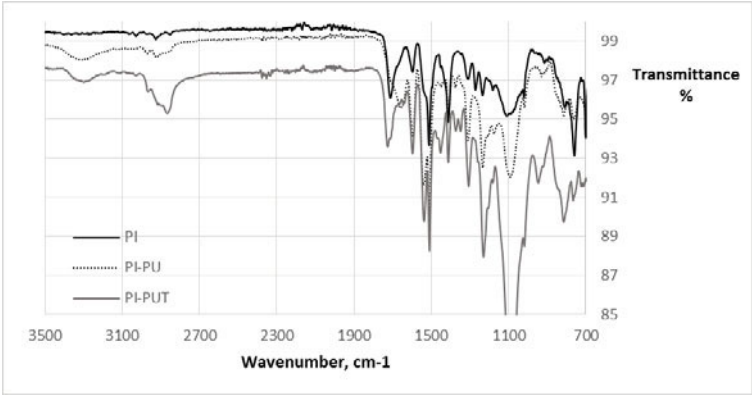

Figure 1. FTIR-ATR spectra of PI, PI-PU and PI-PUT aerogels.

The peak assignment is given in Table I.

Table I. Peak assignment for polyisocyanate aerogels.

Wavenumber (cm-1)	Assignment
1220	C-N urethane; urea [3]
1068; 1225	C-O-C stretching vibrations [4]
1411	Isocyanurate ring [3]
1668	CO-NH vibration urea [2]
1725	OC=O vibration urethane, non-hydrogen bonded [1, 2]
3300	N-H stretching vibration [4]

Thermal Conductivity (TC)

A Design of Experiments study on PI-PU aerogels showed a complex relationship between the properties of aerogels and the formulations. Thermal conductivity and deformation decreased with increasing the aerogels' target density in the 0.04 g/cc to 0.08 g/cc range. Increasing the target density over 0.08 g/cc was undesirable due to a decrease in flexibility. A lower isocyanate/amine ratio led to improved thermal performance and reduced deformation under impact. Optimization of other formulation variables, including the isocyanate functionality resulted in fabrication of flexible PI-PU aerogels with a thermal conductivity of 18 mW/m-K (Figure 2). The thermal conductivity of these aerogels remained unchanged after one cycle of laundering and drying.

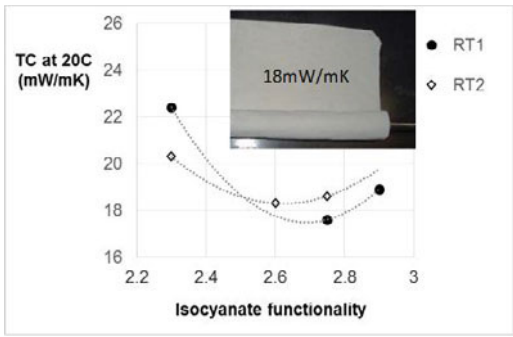

Figure 2. Thermal conductivities of PI-PU aerogels as a function of the isocyanate functionality at short (RT1) and long (RT2) reaction times.

As shown in Figure 3, the fiber reinforced PI-PUT aerogels showed a decrease in thermal conductivity (TC) with increasing the isocyanate index. Increasing the isocyanate index, however, resulted in slightly dustier aerogels.

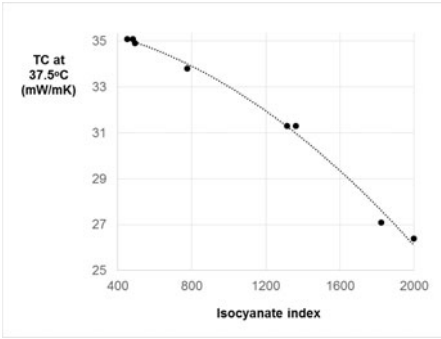

Figure 3. TC of PI-PUT aerogels as a function of the isocyanate index.

Characterization of Physical and Mechanical Properties

A significant improvement over the silica aerogels, these polyisocyanate aerogels showed little, if any, shedding and were deemed suitable for use in apparel. Dust scores for several polyester reinforced aerogel materials were assigned by our subcontractor, Crye Associates, a military apparel fabricator. The PI-PU material showed low enough dust to be handled with the same manufacturing equipment and procedures as textiles (Figure 4).

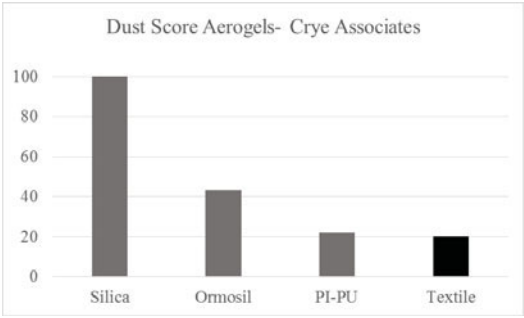

Figure 4. Dust comparison of various fiber reinforced aerogel materials.

The PI-PUT aerogel crosslinked with both polyamine and polyol showed 10 times lower dust compared to PI-PU, measured at Aspen after tumbling with baseballs. PI-PUT aerogels with excellent flexibility and resiliency were prepared using various ratios of polyol to polyamine. Generally, their densities decreased with increasing the hydroxyl/amine molar ratio. As shown in Figure 5, the flexural modulus decreased with the density of the aerogels. Remarkable was

the non-hardening of some of these PI-PUT aerogels at cryogenic temperatures, showing a flexural modulus of less than 0.5 MPa at -130 ºC.

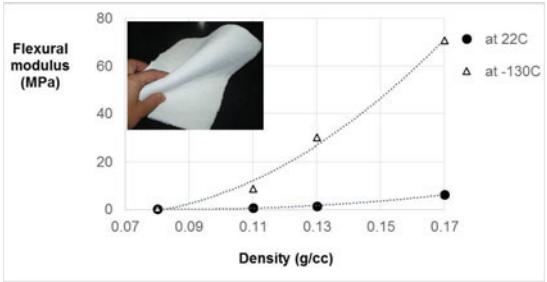

Figure 5. Flexural modulus as a function of density of PI-PUT aerogels at ambient and cryogenic temperatures.

Applications of Polyisocyanate Aerogels

Aspen's PI-PU aerogel was demonstrated in the fabrication of diver gloves for Special Operations Forces. The aerogel integrated glove prototype was tested on a hand calorimeter at the Naval Clothing Textile Research Facility in Natick, MA. At similar thickness, the glove using aerogel outperformed the commercial neoprene foam glove by a factor of 1.6-1.7 in air and by a factor of 2.7 as immersed under water (Figure 6).

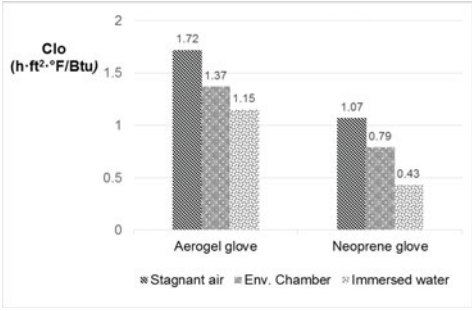

Figure 6. Comparison of total thermal insulation values recorded for the aerogel glove prototype with that of a baseline neoprene wet glove.

The PI-PUT aerogels were investigated for potential use by NASA's astronauts in Extravehicular Activity (EVA) suit assemblies. These highly flexible aerogels were tested for durability over 100,000 cycles by our subcontractor, ILC Dover. A TMG ply-up was modified

by replacing the Multilayer Insulation (MLI) with PI-PUT aerogel. Figure 7 shows the cycling of the aerogel in the Flex tester and the aerogel after testing.

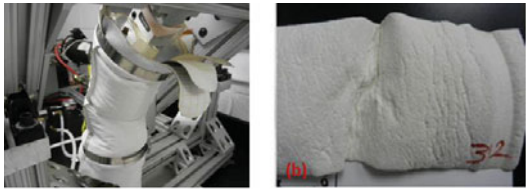

Figure 7. Flex sock apparatus showing cycling of TMG ply-up with PI-PUT aerogel replacing MLI.

There was no sign of dust generation within the TMG, and the materials exhibited adequate resistance to wear and abrasion. Crease lines at the point of bending appeared within the first 100 cycles, but did not propagate throughout the duration of the 100,000 cycle test.

CONCLUSIONS

Flexible polyisocyanate aerogels with excellent durability and textile feel, fabricated at Aspen Aerogels, Inc., showed promise for use in apparel and specialty garments. They were integrated and tested in gloves for extreme cold diving and as MLI replacement for EVA suit assemblies.

These aerogels have high isocyanurate content, PI-PU contains urea crosslinks and PI-PUT has additional urethane groups. The PI-PU aerogels showed 5 times less dust compared to silica aerogels and low thermal conductivities which remained unchanged after laundering. The PI-PUT aerogels with higher flexibility and resiliency compared to PI-PU showed no particulate shedding, good flexural durability and low flexural modulus at ambient and cryogenic temperatures.

ACKNOWLEDGMENTS

The research was supported by the Office of Naval Research under Contracts No. N00014-09-M0009 and No. N00014-10-C-0364 and by the NASA Johnson Space Center under Contract No. NNX12CE92P.

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