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Hollow-microsphere composite offers depth-independent superior thermal insulation for diver suits

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Abstract

We present an experimental proof of principle for a composite material to be used for diver suit insulation. Traditional suits are made of foamed neoprene, which shrinks with increasing pressure at depth under water, leading to a loss in thermal protection for the diver. Our experiments show that the insulance of neoprene from a top-of-the-line 8 mm suit drops by ~52% at 57 psi added pressure (equivalent to 128 FSW depth). In contrast, the insulance of our composite is higher than neoprene's at atmospheric pressure and drops by ~1% at the same 57 psi added pressure. The composite is made of 3 M K1 air-filled glass microspheres embedded in Sylgard 184 silicone. The more than twice better thermal performance of the composite compared to neoprene suggests that there will be a corresponding increase in the persistence time of divers equipped with composite suits. COMSOL theoretical calculations agree with our experimental results, while SEM images of the composite confirm that there is no significant breakage of microspheres during material fabrication. Our results show that the microsphere composite is an excellent candidate to replace bubbled neoprene in diver suits.

1. Introduction

Traditional diving wetsuits are made of closed-cell neoprene foamed with air or nitrogen bubbles [1]. The bubbles make the material thermally insulating, light, and flexible. However, as the swimmer dives deeper, the ambient pressure on the neoprene increases, causing it to shrink accordingly. The thickness of the material decreases, the trapped air is compressed, and the insulation capability and buoyancy of the suit degrade significantly [2]. As hypothermia is a serious health hazard to divers, particularly in cold waters, the decrease of thermal protection with depth is a major problem with foamed neoprene suits.

One approach to solving this problem is to use materials that do not shrink appreciably with pressure. In the 1970s, a few patents emerged that suggested the use of hollow hard spheres [3, 4]. Following the same idea, the US Navy NCTRU at Natick (MA) worked on prototype suits filled with glass microspheres [5]. While these experiments showed improved thermal properties, the suits suffered from tailoring and manufacturing problems, as well as degraded performance attributed to breakage of the microspheres. It appears these issues led to the eventual abandonment of the project.

Some 40 years later, the situation has changed dramatically: inexpensive well-characterized high-quality hollow microspheres have become commercially available and have been studied for materials applications [6–9]. Various techniques of diver suit tailoring and manufacture [1] have been developed. So, the time has come to revisit the approach.

Accordingly, we built a composite material by embedding commercial hollow glass microspheres into polydimethylsiloxane (PDMS). We built a testing station that allowed us to measure the thermal insulance of the material as a function of ambient pressure. We tested our composites and neoprene from a top-of-the-line 8 mm wetsuit. The results showed that between zero depth and 128 FSW (feet of seawater) depth equivalent, the divesuit neoprene loses ~52% in thermal insulance, while our composite typically loses only ~1%. At 128 FSW

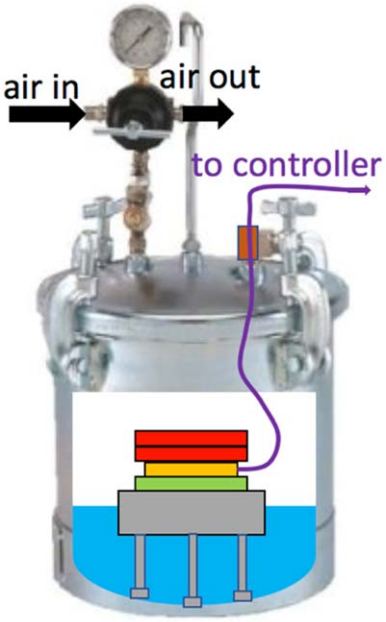

Figure 1. Schematic of the experimental setup (not to scale). A pressure vessel houses a machined aluminum table (gray) wading on adjustable bolt legs (gray) in a mixture of water and melting ice (blue). The interrogated sample (green) is sandwiched between the aluminum table and a heater plate (orange). The plate is insulated on the top by two thick composite discs (red). A cable (purple) connects the plate to a controller box through a fitting filled with epoxy (brown).

equivalent, our composite has ~2.7× the thermal insulance of the divesuit neoprene at the same pressure. These results suggest that our composite is a good candidate for replacing foamed neoprene as the main thermal insulation in diver wetsuits.

We also performed COMSOL simulations of the bubbled neoprene and our composite. They showed that: neoprene's degraded performance is mostly due to shrinkage under pressure; our composite experimental results match the COMSOL predictions; our composite has achieved close to maximal packing of the microspheres without significant breakage. We confirmed the last point directly by SEM images of the composite. No significant breakage means that we have overcome the old problem for such suits, while also demonstrating highly desirable thermal properties.

2. Materials and methods

A. Materials and consumables. Sylgard 184 polydimethylsiloxane (PDMS) 1.1 lbs kits were obtained from Dow Corning through Ellsworth Adhesives, Irvine, CA. K1 hollow glass microspheres were obtained from 3 M. Polystyrene Petri dishes and nitrile gloves were obtained from VWR. The neoprene suit was Aqua Flex SolAfx 8/7 from Aqua Lung.

B. Equipment. The planetary rotary mixer was ARE-310 by THINKY Inc., Japan. The oven was 179 L VWR Forced Air Oven. The balance used was a VWR E-Series 1000 g. The compressor was California Air Tools Model 5510SE (5.5 gal tank, 1HP). The pressure vessel was a BINKS 2.8 gal Paint Tank rated at 80 psi max. Regulators, gauges and pipe fittings were all standard commercial components. The heater stage and controller were manufactured by and obtained from Brook Industries, Lake Villa, IL.

C. Experimental setup. The air compressor was connected by a pressure line to the input of the pressure regulator assembly. The assembly was connected to the input on top of the hatch of the pressure vessel (figure 1). The same assembly also contained an analog pressure gauge. The output of the pressure vessel was plugged with a narrow nozzle fitting, through which the cable between the heater stage and its controller box was passed. The cable was epoxied in position within the fitting to provide hermetic sealing. A simple cylindrical aluminum table was machined in-house.

D. Sample fabrication. Parts A and B from a PDMS kit were poured into a THINKY mixing jar, at the standard curing ratio of A:B = 10:1 by weight, as measured with a VWR balance. Then the lid was closed and the jar was weighed again to determine centrifuge counterweight. The mixture was mixed in the THINKY planetary mixer at 1500 rpm for 4 min. The lid was opened and a varying amount of K1 microspheres was

poured on top of the prepolymer in the jar. The lid was closed and weighed again to determine centrifuge counterweight. The mixture was first mixed at 1500 rpm for 4 min and then degassed at 2200 rpm for 5 min. Then the lid was opened and the mixture poured into a polystyrene Petri dish (137 mm diameter). The Petri dish was placed in a preheated oven stabilized at 80 degC, where the elastomer was allowed to cure for 40 min. The disc-shaped sample was then taken out of the oven, allowed to cool to room temperature, and then extracted from the Petri dish.

E. Experimental procedure. The aluminum table (figure 1) is placed in the pressure vessel and adjusted to be horizontal, using the bolts on its bottom. A mixture of water and ice is poured into the synthetic bucket fitted to the pressure vessel, so that the aluminum table wades in the mixture but the water level does not reach the top surface of the table. The mixture serves as a heat sink. The disc sample is placed and centered on top of the aluminum table. The heater stage is placed on top of the disc sample. Two sample discs (total thickness 18 mm, made out of 49% vol. K1 microspheres in PDMS) are placed on top of the heater. The hatch is closed and its 4 clamps are flipped on, screwed in, and tightened. The power supply of the heater is turned on and the temperature of the heater is allowed to equilibrate to 37.0 degC. Air pressure is gradually increased from 0 to 60 psi relative to atmospheric pressure, in steps of ~2 psi. At every step, the system is allowed to equilibrate for a few minutes and then the input voltage and current readings are recorded. All samples are measured using the same double disc insulation on top of the heater, for a self-consistent and fair comparison. At the end of every experiment, the water/ice mixture is checked to confirm there is still ice in it, ensuring the constancy of the temperature of the heat sink.

F. Measurement of sample thickness. For each disc sample, the sample thickness was obtained by taking the average of the values measured by a metric micrometer at six locations spaced evenly along the circumference of the disc.

3. Results and discussion

We set out to fabricate the microsphere-based composite material, measure its thermal properties, and then compare them to the ones of foamed neoprene. To maximize thermal insulation and minimize weight, we selected the lowest-density hollow glass microspheres commercially available, evidently K1 microspheres by 3 M. K1 have listed specific density of 0.125 g cm^{-3} and crush pressure is 250 psi for 90% survival rate. That pressure corresponds to ~560 FSW depth, whereas wetsuits and semi-dry suits see most of their use at depths smaller than 200 FSW.

We chose Sylgard 184 PDMS as the carrier material for the beads, because it is inexpensive, easy to work with, transparent, and of relatively low viscosity in its prepolymer state. To mix in the microspheres, we used a planetary mixer, which moves the material around a lidded jar, resulting in thorough mixing without the use of stirring blades that can mechanically damage the microspheres. The planetary mixer also provides degassing by centrifugation, thereby helping to avoid the trapping of air bubbles inside the material during thermal curing.

The disc-shaped samples were fabricated with a thickness of ~7 mm to make them comparable to the thickness of a heavy-duty neoprene suit. Their diameter (137 mm) was set by the disposable Petri dishes used as molds to cast the samples. That diameter allowed for sufficient material to extend beyond the edges of the heater plate (110 mm diameter), to ensure minimization of edge effects. Thus, the aspect ratio of the lateral to vertical dimensions for each sample is ~16:1. This ratio prompted us to neglect edge effects and treat the system vertically as one-dimensional for purposes of heat transfer. We also obtained a maximal thickness (8 mm) neoprene wetsuit and cut a sample out of its breastplate to approximately the same diameter as the composite samples. We measured that neoprene sample in the same system, to provide proper comparison.

The operating temperatures of the test station were chosen to mimic the worst-case scenario where a suit-wearing diver with body temperature of 37 degC is exposed to freezing water at 0 degC. Also, using a mixture of ice and water was a straightforward way to ensure the constancy of the temperature of the heat sink, thereby allowing reliable quantitative measurements.

Using the experimental setup (figure 1), we measured the current and voltage needed to keep the heater at 37 degC as a function of applied pressure, for pure PDMS, for the neoprene suit sample, and for a series of composite samples of various %vol of microspheres. Since we wanted to compare the performance of the materials in terms of thermal insulation, the most appropriate parameter to calculate was the thermal insulance Θ (the ratio of the temperature difference to the heat transferred per unit time per unit area):

$$\Theta = \frac{\pi D^2 \Delta T}{4IV} \quad (1)$$

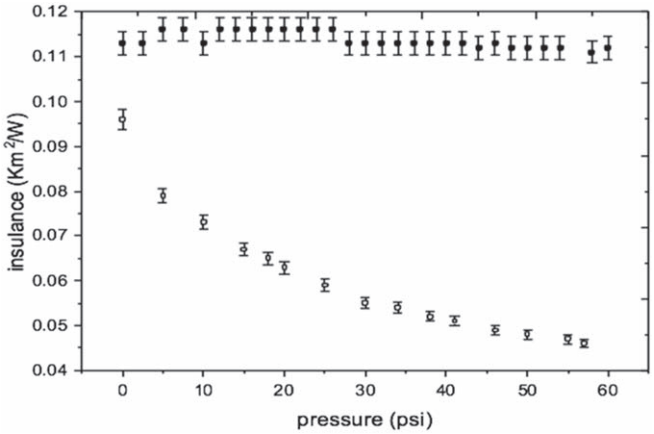

Figure 2. Thermal insulance of 6.5 mm-thick microsphere composite (filled) and 8 mm-thick neoprene (empty) from a top-of-the-line dive suit, as a function of applied pressure.

where D is the diameter of the heater (110 mm), ΔT is the temperature difference between the heater and the melting ice/water mixture (37 degC), I is the current, and V is the voltage. We then plotted Θ as a function of applied pressure. Figure 2 shows the results for the neoprene from the diver suit, and for one of our composite samples.

Figure 2 shows that at atmospheric pressure, the composite (though thinner) already has higher insulance than the neoprene sample. Also, at a 57 psi increase in ambient pressure (128 FSW depth equivalent), neoprene loses ~52% in insulance while the composite loses <1%. Finally, at that depth, the composite system offers a 2.7× better insulance than neoprene. These results show that the composite is a good candidate as a replacement to neoprene as the primary thermal protection in diver suits.

The decrease in heat loss means that it should take longer by the same factor for a diver to cool down from normal body temperature (~37 degC) to the onset of hypothermia (~35 degC) [10, 11]. This means that the persistence time of a diver at depth would be increased by the same factor, at least in terms of the heat limits, if current neoprene suits are replaced with suits made of the microsphere composite.

To optimize the composite experimentally, we built and tested 40 samples of varying microsphere content. Since the material does not shrink appreciably with pressure, we calculated the thermal resistivity by dividing the insulance at 0 FSW by the thickness of the sample. That would allow a fair comparison among samples of varying thickness.

To track content, we calculated the volumetric percentage of microspheres, based on the assumption that there is no significant breakage, so volumes are additive. Then:

$$m = m_p + m_s = \rho V = \rho_p V_p + \rho_s V_s = \rho_p (V - V_s) + \rho_s V_s$$

$$V(\rho_p - \rho) = V_s(\rho_p - \rho_s)$$

Then

$$\alpha \equiv \frac{V_s}{V} = \frac{\rho_p - \rho}{\rho_p - \rho_s} \tag{2}$$

where $\rho_s = 0.125\ \mathrm{g\ cm^{-3}}$ from K1 specs from 3 M, $\rho_p = 1.02\ \mathrm{g\ cm^{-3}}$ by specs for PDMS Sylgard 184 and our measurements of pure polymer samples, and ρ was calculated for each sample from measurements of mass and geometry.

The results are shown in figure 3. Higher volumetric percentage led to higher thermal resistivity of the sample, as expected. As we tried to saturate the material with microspheres, we produced samples that approached but could not exceed 55%. This is above the theoretical maximal packing of identical spheres at ~52% for a simple cubic lattice, since K1 samples contain a distribution of microsphere sizes, which increases packing efficiency. On the other hand, the mixing with pre-polymer makes it practically hard to approach the theoretical limit of ~74% for face-center cubic lattice of identical spheres.

To make sure that our assumption of insignificant breakage is valid, we examined the samples under SEM (figure 4). The results show that indeed while there are a few broken spheres, almost all the spheres appear intact. The surface looks uneven, because we ripped the material apart to expose a fresh surface, instead of cutting it, which would have crushed some of the spheres. Some spheres seem to have slivers on them, which is likely an artifact of making the spheres and/or the tendency of PDMS to crack and rip under extreme stress [12].

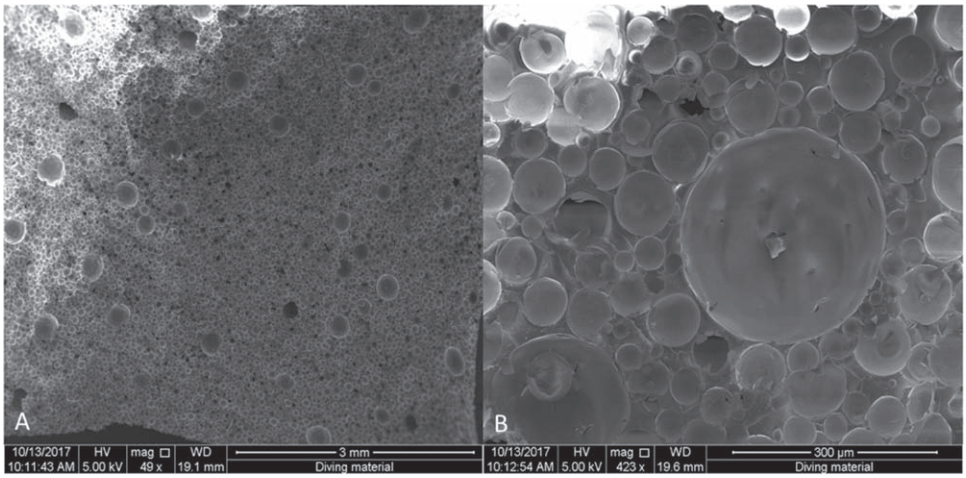

Figure 3. SEM images of the composite. With a few exceptions, microspheres appear intact. The size variation of 3 M K1 microspheres is also evident.

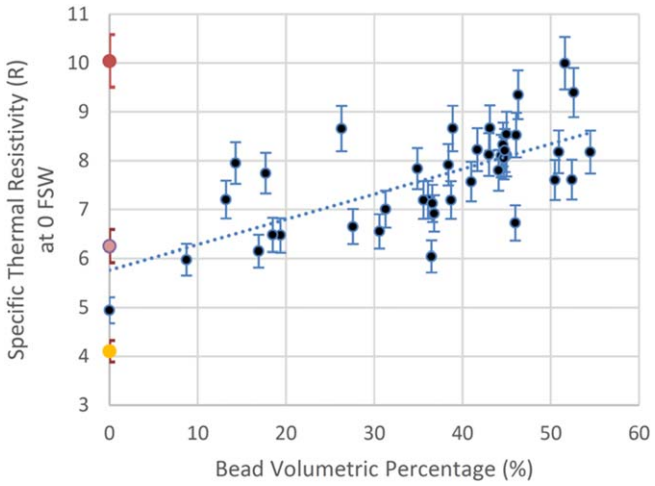

Figure 4. Specific thermal resistivity as a function of microsphere content volumetric percentage, for pure PDMS and for a series of composite samples (blue). For comparison, neoprene is shown at the sea level (red), at 40 FSW equivalent (pink), and at 135 FSW equivalent (orange).

To help theoretically explain our resistivity measurements, we built a model of the composite in COMSOL, which is a widely-used software package for physical model solving and simulations (www.comsol.com). The cubic unit cell contained a single microsphere at its center. As the radius of the sphere was allowed to vary up to the inscribed radius, the simulation scanned through the values of α and calculate the thermal resistivity of the resulting materials. Because resistivity is a bulk property, calculating it for the cubic cell versus a larger sample should produce the same answer. Figure 5 shows the results.

The three curves correspond to different inputted values for the thermal resistivity of the material of the spheres. 'Air' corresponds to neglecting the glass completely and treating the spheres as incompressible but made of air at atmospheric pressure. 'Factory' uses the spec value from 3 M. 'Glass shell' corresponds to COMSOL treating the microsphere as a glass shell filled with air, where the thickness of the glass was calculated based on the 3 M spec for the density of the microspheres, the density of borosilicate glass, and the density of air at atmospheric pressure.

Comparison with the experimental data indicates that the 'air' model overestimated the resistivity. That suggests that glass matters even though the glass shell is very thin. On the other hand, the 'glass shell' model underestimates the experimental resistivity. That may be a result of the model treating all shells as the same size. Large variation in size, e.g. a few very large intact microspheres would increase the overall resistivity of the sample, compared to its apparent α. The best agreement seems to be achieved while using the 'factory' value for the effective thermal resistivity of the microspheres.

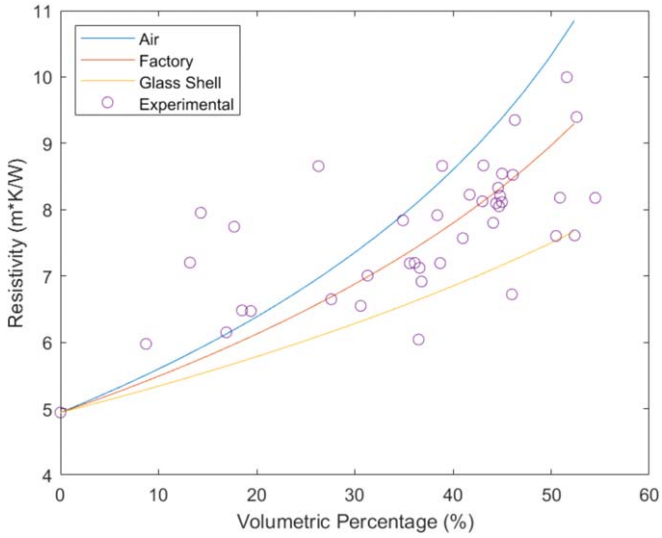

Figure 5. COMSOL simulations calculate resistivity in three models: 'air' where microspheres are treated as incompressible bubbles of air (neglect thin glass); 'factory' uses the 3 M spec for the average resistivity of microspheres; 'glass shell' inputs glass and air resistivity as well as shell thickness calculated through mass density.

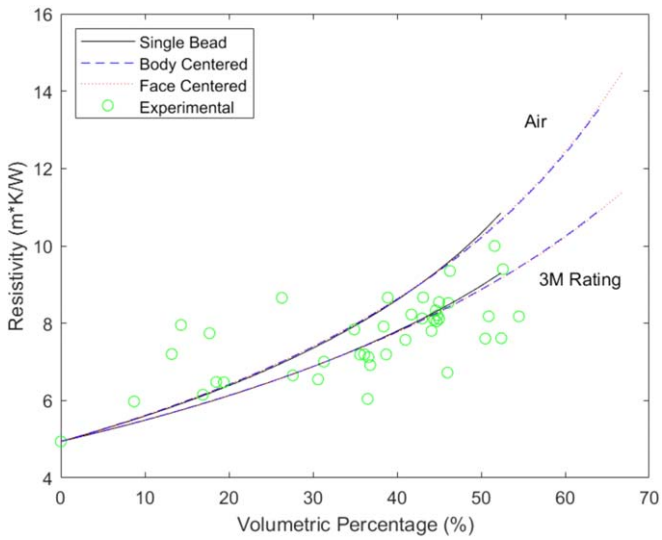

Figure 6. COMSOL simulations calculate resistivity for different lattice arrangements within 'air' and '3 M factory' models.

The COMSOL predictions in figure 5 all use the same geometry of a single sphere centered inside the cubic cell (SSC). To investigate the effect of lattice type, we also ran COMSOL simulations with the same type of microspheres arranged in the cell in body-centered cubic (BCC) and face-centered cubic (FCC) configurations. The resulting curves are shown in figure 6 with the same experimental datapoints presented as circles. The upper family of curves corresponds to the spheres treated as incompressible and made of air (ignoring the thin glass), while the '3 M' family of curves was generated using the 'factory' specified thermal resistivity of the microspheres. The latter seems to be in better agreement with the experimental data. Within the same family, all three lattices behave essentially indistinguishably for $\alpha \leqslant 50\%$, while we have been experimentally unable to exceed 54%. So, while theoretically the FCC and BCC might offer even better results, we are limited in the ability to mix the microspheres with the prepolymer and arrange them for maximal efficiency. The likely solution for even better packing is to have an optimized mixture of microspheres of different sizes.

While the above results already show that the composite is a good candidate to replace neoprene in diver suits, many questions remain and would be subject to subsequent research.

A key question is wearability. Ultimately, a diver must be able to wear the suit and swim. This means it should not be too heavy or too stiff. The 43% composite at 0.53 g cm^{-3} is denser than neoprene but about twice less dense than water. The average surface area of an adult male is 1.9 m^2 [13]. Assuming a thickness of 7 mm results

in total suit weight of ~7.0 kg (15.4 lbs). This is a generous upper bound, because a full suit does not cover the face, hands, and feet, which have particularly high surface-to-volume ratios.

Neoprene is reasonably flexible yet it is tiring for the divers to swim in thick neoprene suits, because the suit resists the bending. As a result, experienced divers minimize the length and speed of their motions. Our composite material is stiffer than neoprene, so that is a problem, particularly as higher α are thermally desirable but increase the stiffness as well.

As one solution, a material even more flexible than PDMS Sylgard 184 (e.g. some versions of GE RTV [14]) could be used as the carrier of the microspheres in the composite. A second solution would be to mix the microspheres with neoprene prepolymer, then foam it with fewer bubbles. That should gain flexibility but at the expense of some of the insulation advantage.

A third solution is to build the suit with segments of variable thickness and/or microsphere content. Most of the surface of the body does not bend significantly. This means those areas would have no problem wearing thicker stiffer slabs of the composite. In contrast, areas that bend much and often, e.g. around major joints, can be covered with a thinner composite of lower microsphere content. Since thermal loss happens through the surface, if ~90% of the body surface is protected 2.7× better and the remaining 10% at comparable level, then the overall protection would be improved by 2.4×.

4. Conclusions

We have experimentally shown that a composite material, made of hollow glass microspheres embedded in elastomer, essentially retains its thermal insulance (loss <1%) up to at least 57 psi positive pressure (~128 FSW depth equivalent), while thicker neoprene from a commercial diver suit loses over half of its insulance. At that pressure, the composite has 2.7 times better insulance than the neoprene. COMSOL theoretical models of the system agree with the experimental results. That agreement and SEM images indicate that there is no significant breakage of the microspheres during material fabrication. Our results suggest that a segmented suit made out of the composite would be a marked improvement over current neoprene suits.

Acknowledgments

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