A Nature-Inspired Superhydrophilic Nano-Powder based Silicone Rubber Composite

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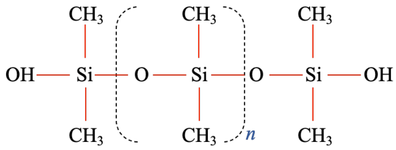
Abstract

Silicone-Rubber (SR) is an elastomer prominently used in biomedical and medical devices, implants, and winter shoe industries because of its stability, durability, friction properties, biocompatibility, anti-bacterial, temperature resistance, and hypoallergenic characteristics. However, inherent hydrophobicity limits the use of SR as it cannot form a protective liquid layer for implants and medical devices while placed internally or externally and impairs tissue adhesion as well. Moreover, hydrophobicity reduces ice adhesion strength in the absence of capillary bridges and that makes winter shoe-soles more slippery. The physical and chemical solutions like oxidation, UV, plasma, corona discharge, gamma radiation, and Laser radiation grafting to turn SR into hydrophilic are either temporary or change the bulk properties of the compounds. We propose an innovative multifunctional SR composite incorporating zirconia and/or titania nanoparticles produced by roller mixing followed by hot compression moulding (pressure/heating vulcanisation). Subsequently, nature-inspired patterns like gecko or frog toepads are produced on SR compound by Laser-Surface-Texturing (LST) to expose the nanoparticles that attract water molecules. A parametric optimisation along with nano-powder percentage decides the wettability of the composite. A permanent superhydrophilic SR compound was produced that can be further used to increase ice adhesion to manufacture anti-slipping winter shoe-soles or other biomedical applications.

Keywords: Nature-inspired, Shoe-sole, Rubber, Laser Surface Texturing (LST).

1. Introduction and Context

Silicone Rubber (SR) is an unreactive, stable, and versatile material because of its excellent properties such as flexibility, high heat resistance and electrical insulating properties. SR is an elastomer made up of silicone that is a synthetic polymer comprised of silicon, hydrogen, carbon, oxygen, and other elements. Silicone polymers cross-link in the presence of catalyst and create three-dimensional bonding network. SR can stand extreme temperatures ranging from − 80°C to 200°C and can be moulded into several geometries and sizes using forming techniques such as extrusion, compression moulding, or injection moulding [1][2].



SR has huge range of applications from automotive, electrical, electronics, aerospace industries to household appliance and cookware to biomedical applications. SR is ideal for biomedical and medical devices, implants, prosthetics, catheters, and tubing because of its chemical inactivity/resistance, odour resistance, biocompatibility, and UV resistance. Accumulation of the bacteria on the surface of implants or organic materials is a widely discussed problem and the anti-bacterial property of the SR makes it an ideal choice. These bacterial infections not only lead to severe contaminations but also depreciation of material [3][4][5].

Apart from the applications mentioned above, a potential solution of the SR can be for shoe-soles that people use for industrial shopfloors where the anti-bacterial properties are desired. Furthermore, hydrophilic SR can also be a good choice if modified accordingly for the winter shoe-soles [6][7] [8].

It is important to discuss the scenarios where hydrophilic SR can present a solution. Because in. spite of all the excellent qualities, poor wear, and wettability limit usage of SR in the palces where capillary bridges are important to consider with the interfacial liquids like in the case of wet ice. Slips and Falls (SF) have been a major challenge during the wintertime while walking on wet or dry ice. These slipping accidents' cost pile up for billions around the world e.g., about 2.4 billion euros annually in Finland, 280 million euros in Sweden, 42 million GBP in UK and the staggering amounts in Canada and USA. Approximately $7 billion capital loss occur because of employees' absence from the workplace around the world due to SF injuries [9][10]. Annually hundreds of thousands of deaths, permanent disabilities, brain injuries and loss of employment is the real face of SF injuries. A capital loss of about $100 billion is estimated worldwide because of SF [11][12][13]. There are several anti-slipping winter footwears available in the market, however, most of them are either based on the material properties or variation in tread patterns to increase friction on ice/snow walking. Other temporary solutions like anti-slipping devices such as spikes, crampons are neither comfortable nor biomechanically optimized. Amount of friction while walking varies from dry ice to wet ice. However, these devices are not fit for people with disabilities, elderlies, and children. Fundamentally, walking on dry ice does not cause much problem, however, melting ice or wet ice is very slippery and cause major trouble [14][15][16][17].

Various chemical treatments can be used to improve the hydrophilicity of silicone rubber (SR), such as UV photo, gamma ray radiation, and laser radiation grafting [16]. Another approach is to blend SR with crosslinked hydrogels or polyacrylamide powders, which are biocompatible polymers with good wettability in various environments. However, their use may be limited due to their frail mechanical characteristics in the swollen state and difficulties in fabrication. To induce water absorptivity, polyalkene oxide PDMS surfactants can be directly introduced into the silicone elastomer matrix [13]. These chemical methods alter the bulk properties of the SR compound and require specialized fabrication techniques, as well as knowledge of vulcanization, crosslinking, chemical affinity of elastomers, and chemistry. Bulk modifications can also involve blending, copolymerization, and Interpenetrating Polymer Networks (IPNs) with the SR, which can change other bulk properties of the compound [9][8][18][19].

Several physical surface modifications can improve the hydrophilicity of silicone rubber (SR). These techniques include flame, corona discharge, gamma rays, UV, ion beam, electron beam, laser, sandblasting, lithography, and plasma. They either introduce oxygen-containing groups or polymerize the surface through crosslinking, resulting in enhanced wettability and adhesion. Compared to chemical methods, physical modifications are easily controllable and precise, and generally do not require any harmful chemicals during or post-processing [20][21][22] [23][24].

Laser Surface Texturing (LST) is a popular technique for creating both hydrophilic and hydrophobic surfaces. Optimal parametric evaluation allows LST to produce permanent hydrophilicity without altering the bulk properties of the surface. Surface modification techniques can either change surface chemistry or impart surface roughness through addition or subtraction of materials. LST, also known as Laser Patterning or Laser Structuring, directly processes surfaces using a laser beam. Unlike other techniques, LST is a single-step, non-contact process that does not require the use of toxic elements. Its non-contacting nature also makes it less prone to contamination. LST can create micro-micro, micro-nano, or nano-nano scale structures, and is a fast and repeatable process that can treat large areas to alter surface roughness and chemistry, thereby modifying surface energy and wettability [25] [26] [27]. The study takes inspiration from frog and gecko to create microfibrillar structures to enhance wettability.

2. Materials

Table 1 and Table 2 gather the properties of SR and Zirconia powder used in the study, respectively.

2.1 Silicone Rubber (SR)

Table 1. Standard characteristics of HCR-SR from Biosil (Primasil Silicone) that can work with the temperature range of –55°C to 200°C. The HCR-SR was tested against Methicillin Resistant Staphylococcus Aureus (MRSA) and E. Coli for anti-bacteria properties according to ISO 22196: 2007 (found ≥99% efficacious).

Physical Properties			
Density	1.10 - 1.20 kg/mm^3	Rebound resilience	52 – 60 %
Hardness	30 – 80 Shore A	Typical Curing Condition	
Tensile strength	7 – 12 MPa	Press-cure	5 minutes @ 160°C
Elongation at breaking	350 – 820 %	Post-cure	4 hours @ 200°C
Tear strength	15 – 30 N/mm	Catalyst	Platinum & Peroxide

2.2 Nano-powder Zirconia

Zirconium oxide used was commercial 3 mol% yttria-stabilized zirconia spray-dried powder purchased from TZ-3YSB-E, Tosoh Corporation, Tokyo, Japan. Table 2 represents the physical and chemical properties of zirconia.

Table 2. Physical and chemical properties of TZ-3YSB-E zirconia nanopowder provided by Tosoh Corporation, Tokyo, Japan.

Physical Properties		Chemical Properties	Weight %
Mass density	6050 kg/m^3	$^{\#}ZrO_2 + H_fO_2 + Y2O_3 + Al_2O_3$	> 99.9
Specific surface area	7±2 m^2/gm	Y_2O_3	5.15± 0.20
Agglomerate particle size	60 μm	Al_2O_3	0.25± 0.10
Crystallite size	36 nm	SiO_2	≤ 0.02
		Fe_2O_3	≤ 0.01
		Na_2O	≤ 0.04

#Calculated value = 100 – ($SiO_2 + Fe_2O_3 + Na_2O$)

3. Methodology

To compound the SR with zirconia nanoparticles, the binder is removed from the micro-agglomerates by heating them in a muffler furnace at 400°C for 30 minutes. The SR compound is prepared using a two-roll mill, where the SR breaks down into smaller crumbs before coming together to form a uniform and homogeneous HCR-SR over a period of 30 minutes. Mixing the nanoparticles before rolling is not preferred as it leads to material loss and non-homogeneous mixing. The process is illustrated in Figure 1(a), (b) and (c).

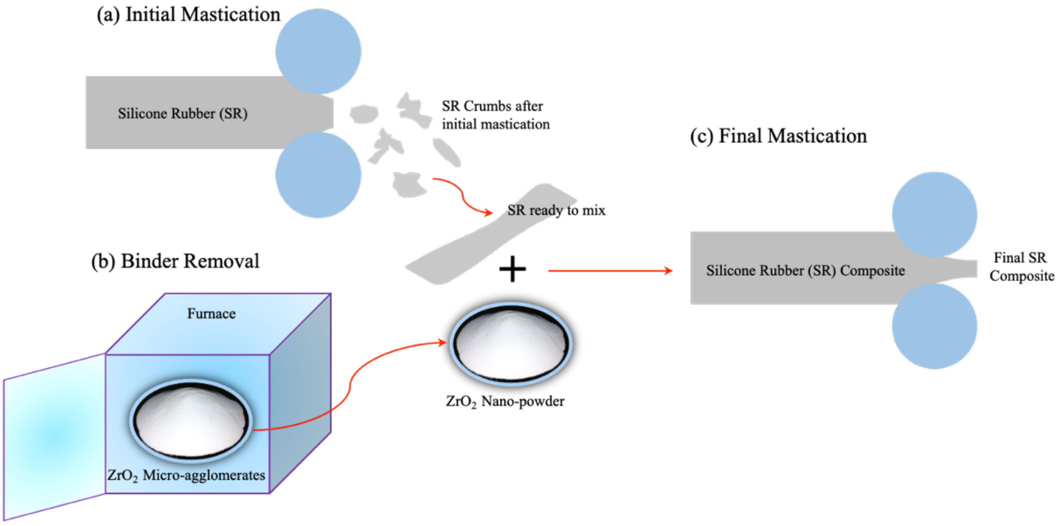


Figure 1: Preparation of SR composite; (a) Initial mastication of SR to remove initial creeping, (b) Binder removal of micro zirconia agglomerate, (c) Final mastication of hand kneaded SR with nanopowder.

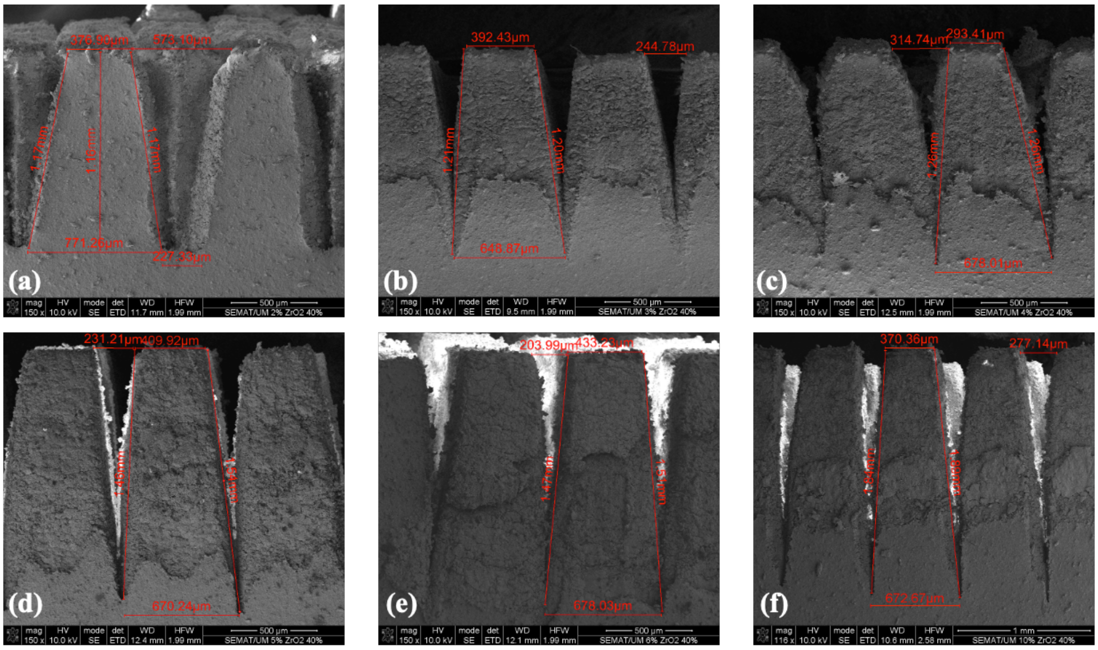


Figure 2: Scanning Electron Microscopy (SEM) images vulcanized silicone rubber with zirconia nano-powders and then textured by Nd:YAG Laser. (a) 2% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages, (b) 3% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages, (c) 4% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages, (d) 5% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages, and (e) 6% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages, and (f) 10% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages.

After the mixing, the prepared composite was vulcanized in a hot compression vulcanization machine under the vacuum. The vulcanization process lasted for 60 minutes at 200°C and 200 MPa pressure. Vulcanized samples with zirconium oxides then Laser textured with the help of Nd:YV04 fibre Laser (Maximum Power of 30 W and spot diameter of 10 microns) as shown in Figure 2. The idea of Laser texture is inherent in the fact that by texturing the surface, oxide powder particles would be exposed and provide hydrophilicity to the rubber. Keeping the hexagonal structures such as frog will extract water from the liquid surface and create capillary effect. This sucked liquid will generate mechanical interlocking. This interlocking will make SR slip resistant and more adherent. The mechanism of mechanical is accompanied by another adhesion phenomenon. A suction cup (inspired by suction cups of octopus' limb) will also be produced by the Laser material removal process at the top of the pillars. These suction cups will induce vacuum and stick to the surface. The adhesion mechanisms of capillary interlocking and suction is important to produce the adhesion.

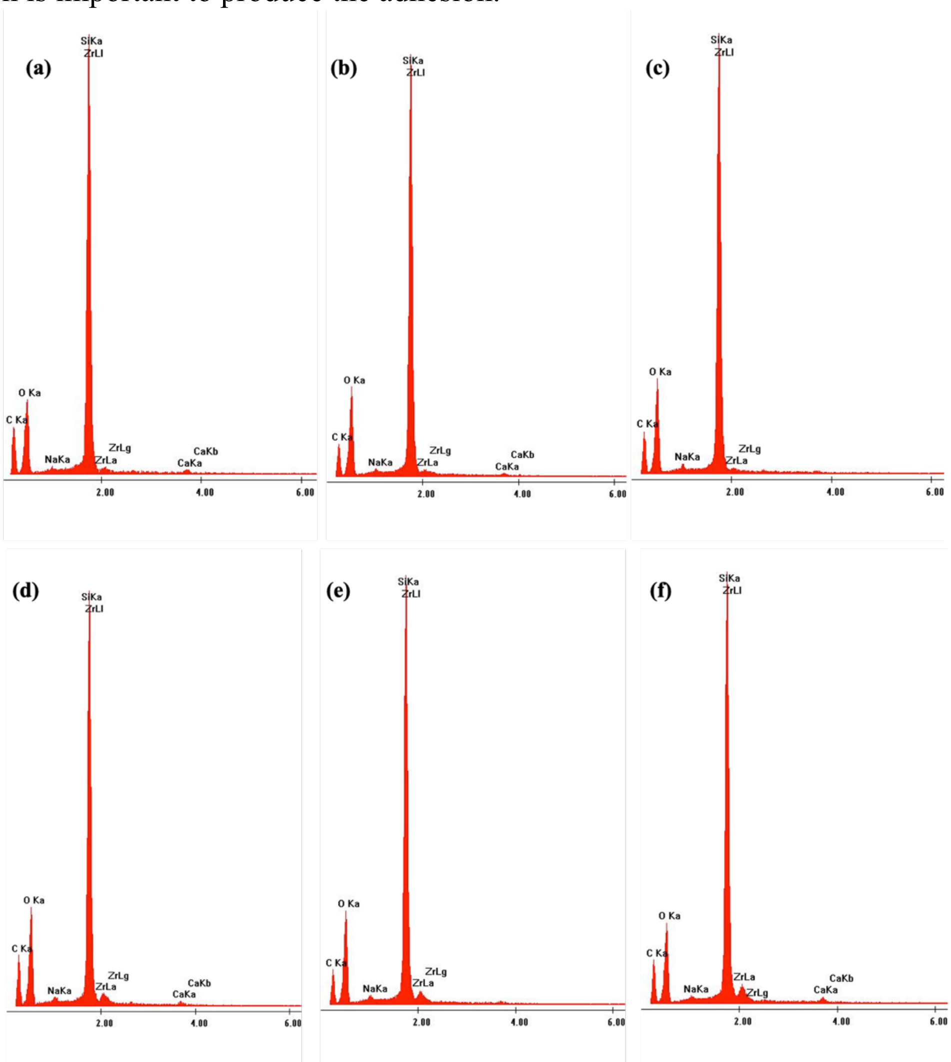


Figure 3: Electron Disperson Spectroscopy (EDS) of all six different percentages zirconia reinforced SR composites at the centre of the pillar. (a) 2% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages, (b) 3% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages, (c) 4% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages, (d) 5% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages, and (e) 6% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages, and (f) 10% by weight zirconia textured at 12 watts, 1000 mm/sec scanning speed, and 100 passages.

Producing capillarity effect by the virtue of wettability is the main aim of this work. The same textures are performed for titania nanoparticles as well and those will lead to other hydrophilic results. It is evident from the Figure 2 that more zirconia nanoparticles mean more depth of the textures and better exposure of zirconia. The exposed zirconia would attract liquid and will decrease contact angle in turn raising hydrophilicity.

Results and Discussions

Zirconia reinforced SR has been vulcanized and superhydrophilicity was obtained using LST. Different oxides create different kinds of wettability in the rubber. The textures engraved by Laser is also the design of tread pattern or channels between the hexagonal projections inspired from the nature. It is evident from the SEM images that oxide particles are present on the vulcanized rubber surface. Figure 3 shows Electron Dispersive X-ray Spectroscopy (EDS) spike diagram to see the presence of oxide powder particles. Tests to perform the same process with titania are being done. Figure 4 shows the results that were obtained after LST for the prepared SR-Zirconia composite. From. Figure 4 (a) and (b) can be observed that by introducing the zirconia nanoparticles, the contact angle θ increases and wettability of the surface increases.

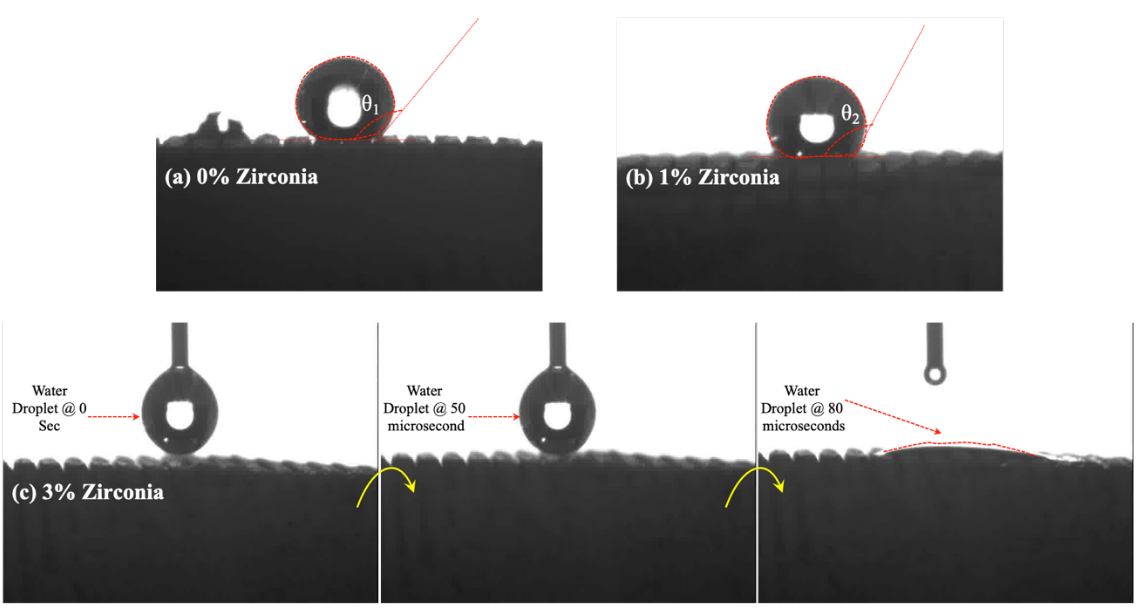


Figure 3: Wettability contact angle measurement; (a) 0% or Without zirconia SR, (b) 1% by weight zirconia composite, (c) 3% by weight zirconia composite.

By further increasing the amount of zirconia up to 3%, it has been found that water droplet completely vanished into the textures within 80 microseconds. The contact angle loses its significance in that case because the case can be considered as the case of capillarity rather than wettability. The surface observed in Figure 4(c) is a case of superhydrophilic surface. Furthermore, higher percentages of zirconia result the same effect as there is no contact angle.

Conclusions

(1) SR composite with zirconia proved to be better for wettability of the surface.
(2) LST exposes the zirconia nanoparticles which increase wettability of the SR composite which in turn gives more capillarity.
(3) The machinability of the SR increases by adding the zirconia nanoparticles.
(4) By adding oxides, wettability can be imparted on the rubber which is hydrophobic by nature.
(5) LST are inspired from the microfibrillar structures of the frog toepad and gecko feet. Furthermore, the adoption from the nature can be proved to a potential source of application.

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