

Superhydrophobic Thermoset Elastomers with Excellent Stability to Rain Erosion and Water Immersion

E. Kujan^{†*}, B. Farshchian[†], Q.F. Xu[†], M. Feldman[‡] and A.M. Lyons^{†‡*}

[†]ARL Designs LLC, Staten Island, NY beth@arldesignsllc.com

[‡]College of Staten Island, City University of New York alan.lyons@csi.cuny.edu

ABSTRACT

Thermoset rubbers with superhydrophobic surfaces would be beneficial for industrial applications such as electrical insulators [1,2] low-slope roof membranes [3,4], and seals [5] because their surfaces are self-cleaning and remain dry when exposed to weather. However most superhydrophobic surfaces are expensive, fragile and are damaged by heavy rain or when submerged in water. To address this need for improved materials, ARL Designs has developed a low-cost method for modifying commercially available elastomers during molding to make their surfaces superhydrophobic with durable properties.

This paper outlines two methods for accelerated testing of the long-term quality of superhydrophobic surfaces that were designed to be robust under real-world conditions. Commercially available thermosetting elastomers, including silicones, a fluorinated co-polymer, nitrile and EPDM rubbers, were treated to render their surfaces superhydrophobic. An accelerated rain erosion test was developed, which simulates natural rainfall, and was used to assess the relative durability of the surfaces as well as understand wear mechanisms. Immersion tests were conducted under 1 meter of standing water. A silicone and a fluorinated co-polymer exhibit the most stable superhydrophobic properties that have yet been reported, withstanding the equivalent of 60 years of annual precipitation as well as over 20 days of immersion under one meter of water.

Keywords: thermoset, rubber, durability, superhydrophobic, elastomer

1 INTRODUCTION

Silicone elastomers are especially well suited to shed water on high voltage terminations because of their hydrophobicity and stable electrical properties [1,2]. However the reliability of silicone insulator components for high voltage applications is reduced in wet conditions compared to dry conditions. This is especially true for heavily polluted or marine environments where dirt accumulation on the silicone surfaces can create sites with high leakage currents, heating, flashovers and, eventually, failure. A superhydrophobic self-cleaning surface would significantly improve performance in wet weather.

Elastomers account for ~25% of the low-slope roof membrane market. Traditionally, these flexible membranes

are made by calendaring EPDM rubber into sheets, curing, and then using an adhesive to bond overlapping sections together. To reduce the solar heat loads trapped by these dark membranes, white roofing with high albedo is required [3,4]. Over time, white roofing membranes become soiled, losing their reflectivity and effectiveness. A self-cleaning superhydrophobic surface would keep such roofing materials clean and reflective.

Elastomers are also used as seals under long-term exposure to rain or immersion in water [5]. For such applications, a superhydrophobic elastomer surface would greatly reduce polymer-water contact, thereby significantly reducing the rate at which some elastomers degrade.

Although commercial superhydrophobic coatings are available, their reliability has not been sufficient for long-term applications outdoors. These add-on coatings are too fragile, expensive or they easily transition from the superhydrophobic (Cassie) state to the wetted (Wenzel) state under heavy rain or when submerged under water. ARL Designs (ARLD) has developed a process that produces the most stable superhydrophobic surfaces that have yet been reported. In this process nanoparticles are partially embedded into the elastomer, creating a mechanically and chemically robust surface that exhibits excellent self-cleaning properties.

2 EXPERIMENTAL

Sample preparation, materials and two durability tests – rain erosion and static immersion - are discussed.

2.1 Materials

Nanoparticles were added to commercially available elastomers during molding at temperatures and times recommended by the manufacturers. A nanoparticle-elastomer composite with hierarchical roughness is formed. The superhydrophobic nanocomposite is integral with the molded object and so is “built-in” to the surface during molding. It is not applied or adhered afterwards.

Elastomers from three suppliers, Parker-Hannifin, Dow-Corning and Wacker Silicones were evaluated. The three elastomers from Parker-Hannifin were: Vinylidene Fluoride-Hexafluoropropylene Copolymer Rubber (V4208-90), Carboxylated Nitrile Rubber (N4257-85), and EPDM Rubber (E4259-80). All were molded at 188°C for 7 mins at 400 psi (800 psi for nitrile). The copolymer was post-cured at 230°C for 16 hrs. The Dow-Corning silicone, XIAMETER® RBC-1760-65, was molded at 171°C for 30 mins at 50 psi. The Wacker Silicone, a low-viscosity

liquid, was molded at 165°C for 15 mins. Disks measuring 100 mm diameter and ~5 mm thick were prepared using a mold of the same size.

2.2 Rain Erosion Test

To assess the stability of the molded superhydrophobic elastomers for outdoor applications, a rain erosion test was developed. In the superhydrophobic literature, there are few published reports concerning rain resistance and immersion stability of materials. Droplet impact studies have examined the effect of relatively large individual drops impacting at velocities well below those of rain [6,7]. No wear is expected under these conditions. One report studied water droplets impacting superhydrophobic surfaces at very high velocities (25 m/sec), which are relevant to turbine blade testing [8]. Such surfaces [8] were observed to transition to the wetted (i.e. Wenzel) state within a few seconds. Maintaining superhydrophobicity under long-term exposure to natural rain (impact velocities of 1-6 m/sec) has not been published.

The challenge with simulated rain erosion testing is to form droplet streams that induce accelerated ageing while using realistic conditions. Unfortunately, the standards for rain exposure testing of materials are not well established. Droplet size and velocity is important to control; rain containing droplets that are too small or impact too slowly will not erode the surface sufficiently whereas large and/or high velocity droplets will induce erosion mechanisms not seen in nature.

Naturally occurring rainfall consists of a broad distribution of droplet sizes and impact velocities. Because of the inherently broad distributions, seasonal and geographical variability as well as measurement challenges, simple averages raindrop diameter and velocity are not easily calculated. An average droplet diameter of 1.5 mm with an impact velocity of 5.3 m/sec has been reported [9] and these values are similar to other studies [10,11]. Approximately 90% of these droplets are < 2.1 mm.

For this study, we used two different nozzles for rain erosion testing. One nozzle is specified in the UL-50 standard test [12]. The other nozzle (BETE MP375NN), shown in Figure 1, provides a distribution of droplets with size, size distribution and velocity that closely approximate natural rainfall [13-15].

To characterize the droplet streams, a high speed video camera (V7.3 Phantom, 6504 fps) was used with the appropriate illumination (Figure 2) to capture still images of droplets as shown in Figure 3. Droplet diameters were calculated by measuring the number of pixels across the drop and comparing to the ruler within the same frame. Droplet velocities were calculated from the number of frames required for the droplet to translate a distance of 18 mm. Average droplet diameters and velocities (based on ~800 measurements) generated by the two nozzles are shown in Table 1 and compared to a value for natural rain.

According to our measurements, the size of droplets produced by the UL-50 nozzle are close to natural rain in size, but lower in velocity. Although lower in energy than

average rain, the nozzle is part of standard and readily available; thus a good source for comparisons. The MP375NN nozzle from BETE, operated at 4 psi, was found to provide a droplet size and velocity distribution that overlaps well with the average diameter and velocity observed in nature and is comparable to the best rainfall simulators described in the literature[13], while being convenient to use in lab tests.



Figure 1: Rain test of a thermoset rubber using BETE nozzle.



Figure 2: High speed camera with backlight used to image droplets.

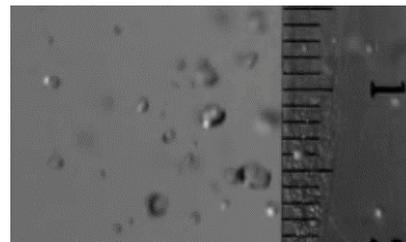


Figure 3: Example frame used to measure size and velocity of simulated rain droplets.

Table 1: Droplets for Rain-Induced Erosion Test compared with Natural Rain [9-11].

Source	Diameter (mm)	velocity (m/s)	Rate
UL-50 at 5 psi	1.5 ± 0.5	3.0 ± 0.1	124 mm/min
BETE at 4 psi	1.5 ± 0.9	5.2 ± 0.6	200 mm/min
Natural rain[9]	1.5	5.3	1300 mm/yr

The droplet size distribution for the BETE nozzle was calculated and the number average droplet diameter and velocity were 1.5±0.9 mm and 5.2±0.6 m/s respectively. The most frequently observed droplet diameter was 1.0 mm. The BETE nozzle provides significantly accelerated conditions as the precipitation rates are high while the droplet diameter and velocity are comparable to those found for natural rain. At a precipitation rate of 200 mm/min

(7.75 inches/min), less than 7 minutes of exposure is required to approximate one year of rainfall in New York City (49.9 inches/year) [16].

2.3 Static Immersion Test

Similar to rain erosion testing, few publications address the challenge of long-term immersion stability of superhydrophobic surfaces. A common belief amongst researchers is that the plastron of a superhydrophobic surface is inherently unstable under water over long times as the trapped air is expected to dissolve into the bulk fluid. Our results clearly show that the plastron can be stabilized as our samples remain superhydrophobic for extended periods (weeks) of time.

To assess the stability of the ARL Designs treated elastomers under water, a 1-meter immersion test conforming to IEC60529-IPX7-8 [17] was built using an 80 gallon polyethylene tank; see Figure 4. The persistence of the air layer trapped between the water and elastomer (i.e. plastron) was verified periodically by bringing the samples close to the surface so that the presence of the highly reflective liquid-air- interface could be visually observed. Care was taken to keep the samples submerged at all times so that the air in the plastron would not be replenished.



Figure 4: Immersion of treated and untreated samples at depth of 1 meter under water.

3 RESULTS

Accelerated test results are discussed.

3.1 Rain Erosion Test

The static contact angles (CAs) and sliding angles (SAs) of water droplets on the surfaces were measured as a function of rain erosion test time. After fabrication, the CAs of 5 μ L water droplets on the Parker elastomers increased from 102°, 90° and 101° to 160°, 156°, and 155° for the copolymer, nitrile and EPDM respectively. The CA values remained stable throughout the rain erosion test.

The angle at which the sample must be tilted for a droplet to slide-off (SA) was also measured throughout the rain erosion test to quantify the stability of the superhydrophobic properties. As shown in Figure 5, the SA values were \sim 2° for the as-prepared samples. The ARL Designs treated Parker co-polymer elastomer proved to be exceptionally stable under rain erosion; the SA remained unchanged for the first 5 hours of test. This is equivalent to approximately 30 years of rain. The sample did not

transition to the wetted state until 13 hours of test (\sim 70 years of rain accumulation). The Nitrile and EPDM from Parker exhibited stability, but were more sensitive to rain erosion compared to the copolymer as shown in Figure 5.

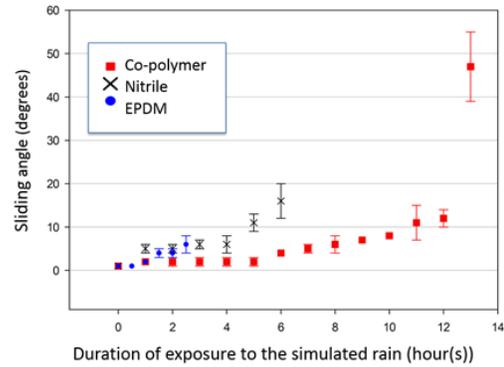


Figure 5. Sliding angle of treated Parker elastomers measured as a function of rain erosion exposure time using a UL-50 nozzle.

Rain erosion testing was conducted on all ARLD treated elastomers with the BETE nozzle using the same procedure. Time to failure was determined when the impinging water droplets wetted the treated surface (i.e. a transition from the Cassie to Wenzel state was observed.). A histogram of the superhydrophobic stability (measured as time to wetting and equivalent years of rain) is shown in Figure 6. All samples remained superhydrophobic for over 1 hour of rain exposure (\sim 10 years of NYC rain). The fluorinated copolymer elastomer from Parker-Hannifin exhibits the greatest stability, enduring 7 hours or \sim 60 years of simulated rain exposure. The Dow-Corning elastomer also performed well, enduring almost 6 hours (48 years) of rain erosion.

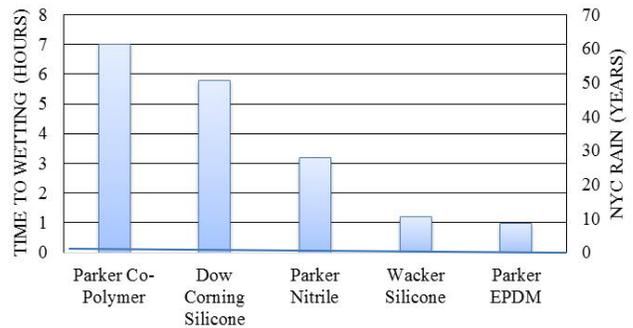


Figure 6. Stability of ARLD treated elastomers measured as a function of rain erosion exposure time using the BETE nozzle. One hour of testing is equivalent to 9.4 years of precipitation in New York City.

3.2 Immersion Test

The ability to maintain superhydrophobic properties while the molded elastomer is submerged underwater is important for maintaining a dry and clean surface. The histogram in Figure 7 shows the plastron longevity for all five different treated samples under static water immersion.

All materials far surpassed the 0.5 hour IPX7-8 standard. The Dow silicone and Parker co-polymer elastomers performed extremely well; the plastron air layer on these samples was maintained for ~3 weeks under water.

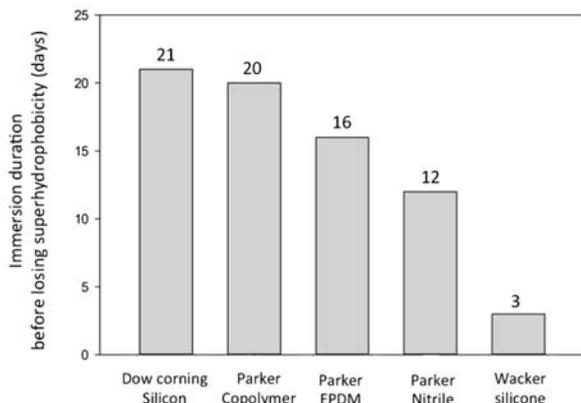


Figure 7: Stability of the plastron (trapped air layer) on ARLD treated elastomers during continuous water immersion at a depth of 1 meter as measured by the number of days before transition from Cassie to Wenzel observed.

This stability is superior to any other superhydrophobic material previously reported. The air layer in the plastron of these ARLD treated surfaces was preserved and so did not dissolve into the 80 gallons of water in which the samples were immersed. These results demonstrate that stable superhydrophobic properties can be achieved under water when the surface is prepared using a chemically stable hydrophobic polymer formed with a suitable nano-scale hierarchical surface roughness.

4 CONCLUSIONS

ARL Designs has developed a scalable process for creating superhydrophobic surfaces onto a wide variety of commercially available elastomers. A nano-scale hierarchical roughness is built into the surface of the cross-linked elastomer through the addition of nanoparticles during the molding process. All of the treated elastomer surfaces exhibit excellent superhydrophobic properties, with contact angles $> 155^\circ$ and slip angles $< 5^\circ$.

Moreover, the ARL Designs treated surfaces show excellent durability. A rain erosion test was established where droplets comparable to natural rain (average diameter 1.5 ± 0.9 mm with velocity of 5.2 ± 0.6 m/sec) were impinging on the surface at a highly accelerated precipitation rate of 200 mm/min.

Elastomers that are both inherently hydrophobic and chemically stable exhibited the most durable superhydrophobic properties. The vinylidene fluoride-hexafluoropropylene copolymer from Parker and silicone from Dow-Corning exhibited the most stable properties, resisting rain erosion for 7 and 5.8 hours (equivalent to 60 and 55 years of New York City rainfall) respectively and over 20 days immersed under 1 meter of standing water. To our knowledge, this level of stability exceeds the

performance of all other superhydrophobic materials reported in the literature.

ACKNOWLEDGEMENTS

E.K., B.F., Q.F.X., and A.M.L. acknowledge support from the National Science Foundation SBIR Phase II program (Scratch and Abrasion Resistant Superhydrophobic Polymer Coatings, Contract: 1330949). Additional support from the CUNY Center for Advanced Technology is appreciated. We thank Daniel Baxter from Parker-Hannafin for providing samples of the co-polymer, nitrile and EPDM elastomers and Janet Jones from R.D. Abbott for the Dow-Corning sample.

REFERENCES

- [1] G. Simson, Nov. 30, 2014 <http://www.inmr.com/2014/11/silicones-offers-better-solutions-cable-accessories-2/>; accessed Nov 30th, 2014.
- [2] Editorial Staff, June 17, 2014 <http://www.inmr.com/2014/06/silicone-insulators-come-dominate-chinese-transmission-lines/>; accessed Nov 30, 2014.
- [3] W. Miller, M. Cheng, A. Pfiffner, N. Byars, ORNL/TM-2002. Oak Ridge, TN, Oak Ridge National Laboratory. 2002 available through The Single-Ply Roofing Institute.
- [4] J. Wilen Professional Roofing 7/2012 34-38; available through <http://www.nrca.net/>
- [5] Parker Hannafin Website. <http://ph.parker.com/us/en/seals-and-o-rings>; accessed Nov 29th, 2014.
- [6] P. Tsai, S. Pacheco, C. Pirat, L. Lefferts, D.Lohse, *Langmuir* 2009, 25, 12293
- [7] L. Zhu, P. Shi, J. Xue, Y. Wang, Q. Chen, J. Ding, and Q. Wang, *ACS Appl. Mater. Interfaces* 2014, 6, 8073–8079
- [8] A. Davis, Y.H. Yeong, A. Steele, E. Loth, *I.S. Bayer RSC Adv.*, 2014, 4, 47222
- [9] A.N. Dingle, Y. Lee, *J. Applied Meteorology*, 1972, 877-879.
- [10] C. Williams, K. Gage, *Annales Geophysicae*, 2009, 555-567.
- [11] G.W. Lee, A.W. Seed, and I. Zawadzki, *J. Applied Meteorology and Climatology* 46.6 (2007): 742-56.
- [12] Enclosures for Electrical Equipment, Environmental Considerations UL50E; September 04, 2007
- [13] T. Iserloh, J. Ries, J. Arnáez, et. alia, *Catena*, 2013 100–112.
- [14] I. Abudi, G. Carmi, P. Berliner, *Journal of Hydrology*, 2012, 76-81.
- [15] P. Khare, T. Agarwal, S. Ghosh, *Journal of Irrigation and Drainage Engineer*, 2014, 140-143.
- [16] Dept of Commerce>NOAA>NESDIS>NCDC> Climate Data Online Dataset Discovery <http://www.ncdc.noaa.gov/cdo-web/datasets>; Accessed Nov 25, 2014.
- [17] International Electrotechnical Commission International Standard, IEC60529, 1999.