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Bioinspired Surface Treatments for Improved Decontamination: Raspberry Microstructures

Brandy J. White

Laboratory for the Study of Molecular Interfacial Interactions
Center for Bio/Molecular Science & Engineering

Brett D. Martin

Martin H. Moore

Anthony P. Malanoski

Brian J. Melde

Laboratory for Biosensors and Biomaterials
Center for Bio/Molecular Science & Engineering

Carissa M. Soto

Formerly, Laboratory for Biosensors and Biomaterials
Center for Bio/Molecular Science & Engineering

Chanté Campbell

Howard University
Washington, DC

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Brandy J. White, Brett D. Martin, Martin H. Moore, Anthony P. Malanoski, Brian J. Melde, Carissa M. Soto*, and Chante Campbell**

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*Formerly, Center for Bio/Molecular Science & Engineering; Naval Research Laboratory, 4555 Overlook Ave., S.W., Washington, DC 20375-5320
** Howard University, 2400 6th St NW, Washington, DC 20059

14. ABSTRACT

This effort evaluates bioinspired coatings for use in a top-coat type application to identify those technologies that may improve decontamination capabilities for painted surfaces. This report details results for evaluation of coatings composed of raspberry microstructures on paintedsurfaces. Retention of the simulants paraoxon, methyl salicylate, and diisopropyl fluorophosphates following treatment of contaminated surfaces with a soapy water solution is reported. Wetting behaviors and target droplet diffusion on the surfaces are also discussed.

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EXECUTIVE SUMMARY

The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) initiated a program in January 2015 for evaluation of bioinspired treatments suitable for use as a top coat on painted surfaces with the intention of achieving improved aqueous decontamination of these materials. Funding was provided by the Defense Threat Reduction Agency (DTRA, CB10125). This report details results for evaluation of top coat applications based on microstructured, reentrant surfaces, also known as raspberry structured. The coatings are based on the use of composite microparticles combining nanospheres of two sizes with fluoropolymer functionalization. Materials were deposited on polyurethane paint coated aluminum coupons. Retention of the simulants paraoxon, methyl salicylate, and diisopropyl fluorophosphate following treatment of contaminated surfaces with a soapy water solution is reported along with droplet diffusion on the surfaces and wetting angles.

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BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: RASPBERRY MICROSTRUCTURES

INTRODUCTION

The DoD Chemical and Biological Defense Program (CBDP) seeks to provide protection of forces in a contaminated environment including contamination avoidance, individual protection, collective protection, and decontamination. In January 2015, the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) began an effort funded through the Defense Threat Reduction Agency (DTRA, CB10125) intended to evaluate top-coat type treatments suitable for application to painted surfaces for reduction of chemical threat agent retention following standard decontamination approaches. The effort sought to survey relevant and related areas of research and evaluate identified technologies under appropriate methods to determine efficacy, scalability, and durability. The current document summarizes results for one type of identified technology, surfaces coated with raspberry microstructures.

Raspberry microstructures are assembled using microbeads of two sizes to provide the sharp transitions (re-entrant surfaces) necessary for producing a superhydrophobic coating on a flat surface.[1] The approach has been shown to produce sliding and shedding angles of <1° for water and diiodomethane and <15° for hexadecane and cooking oil. Microspheres of 0.2 to 5 μm with epoxy and amine surface groups (commercially available) are coupled. The remaining amine groups are removed through acrylation. Copolymers are synthesized on the particles to produce alternating 2-(perfluorooctyl)ethyl and 2-hydroxybutyl branches. The fluorinated units combine with the raspberry-like structure to produce the desired wetting behavior and the hydroxyl groups provide sites for crosslinking to the surface, for example, using polyisocyanate.

This work evaluated different synthetic approaches with varied deposition, component ratios, and loading densities. While no single material has been fully characterized, the breadth of the work presented here demonstrates the unfitness of these raspberry surfaces for producing the desired performance characteristics when used as a top-coat treatment over a painted surface.

METHODS

While the originally published protocol utilized silicate microbeads, polystyrene beads are used here. Two approaches were considered. In the first, EDC chemistry is used to couple amine- and carboxylate-derivatized polystyrene beads in an aqueous suspension to form the raspberry particles. Once the multi-sphere clusters are formed, acrylate groups are attached to the surface. This is accomplished by derivatizing the clusters with glycidyl methacrylate (an epoxide) to form a covalent attachment with the carboxylates via the epoxide. Finally, the beads are placed into an appropriate solvent for polymer chain growth and attachment (Figure 1). Two choices are short-chain fluorinated alcohols and alkyl ethers. These provide full solubility for the co-monomers (compounds such as 1,1,1,3,3,3 hexafluoroisopropyl methacrylate and 4-hydroxbutylmethacrylate) but do not dissolve the raspberry particles. To initiate the free-radical polymerization, azo-bis-isobutyronitrile (AIBN) was activated at 65 °C, well below the melting point of polystyrene. Particles having different ratios of co-monomers were synthesized and characterized using DLS and viscometry. The polymer-grafted microparticles were cast onto glass and/or painted surfaces in the presence of a polymer containing reactive isocyanate side groups (Bayhydur® from Bayer, Inc.). This provides the mechanisms for crosslinking the microparticles onto the support via hydroxyl groups.

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In the second approach, a copolymer containing epoxide and fluoroalkane functionalities is used to crosslink the amine and carboxy groups on the microspheres to form raspberry-type structures, and introduce a low-surface energy coating (Figure 2). The epoxide is present in the copolymer C, based on glycidyl methacrylate and the fluorinated repeat unit 1,1,1,3,3,3 hexafluoroisopropyl methacrylate. The copolymer will also graft onto the microsphere surfaces in a non-crosslinking mode with the fluorine-containing groups producing low surface energy. Here, the epoxide linkage chemistry is catalyzed by trialkylamines, though other catalysts can also be used. For clarity, attached polymer brushes are not shown in Figure 2. Finally, the epoxide functionality is used to crosslink the raspberry-type structures to the hydroxyls present on surfaces. Boron trifluoride is used to catalyze the epoxide linkage.

Fluorinated alcohols and diethylene glycol diethyl ether were identified as the most suitable solvents. In a typical reaction, co-monomer is introduced at a concentration of 10% to 25%, and AIBN is used as initiator at a concentration of 0.5 wt% relative to co-monomer. Overnight, a highly viscous solution is formed, indicating the presence of moderate to high molecular weight polymer. The mole ratio of glycidyl methacrylate to fluorinated co-monomer can be varied to produce differing results. Thin films on glass for the varied materials were formed by casting the glycidyl methacrylate/trifluoroethyl methacrylate copolymer providing water contact angles in the range of 100° to 110°.

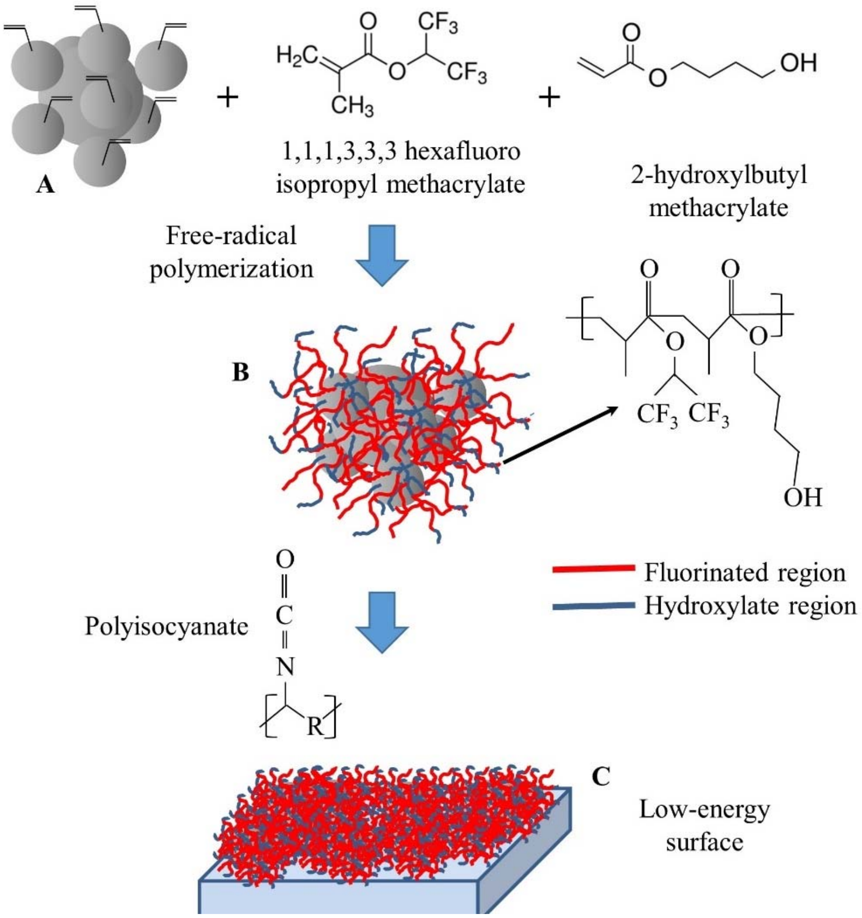


Fig.1. Growth of polymer chains from the surface of acrylate-derivatized raspberry particles (A). Fluorinated comonomers such as 1,1,1,3,3,3 hexafluoroisopropyl methacrylate are reacted with 2-hydroxybutyl methacrylate to form copolymers that are grafted onto the raspberry structures (B). The fluorinated groups provide low surface energy and the hydroxyls allow the structures to be covalently attached to the painted surface (C) via an isocyanate linkage, provided by a poly(isocyanate) linkage such as Bayhydur®, from Bayer, Inc.

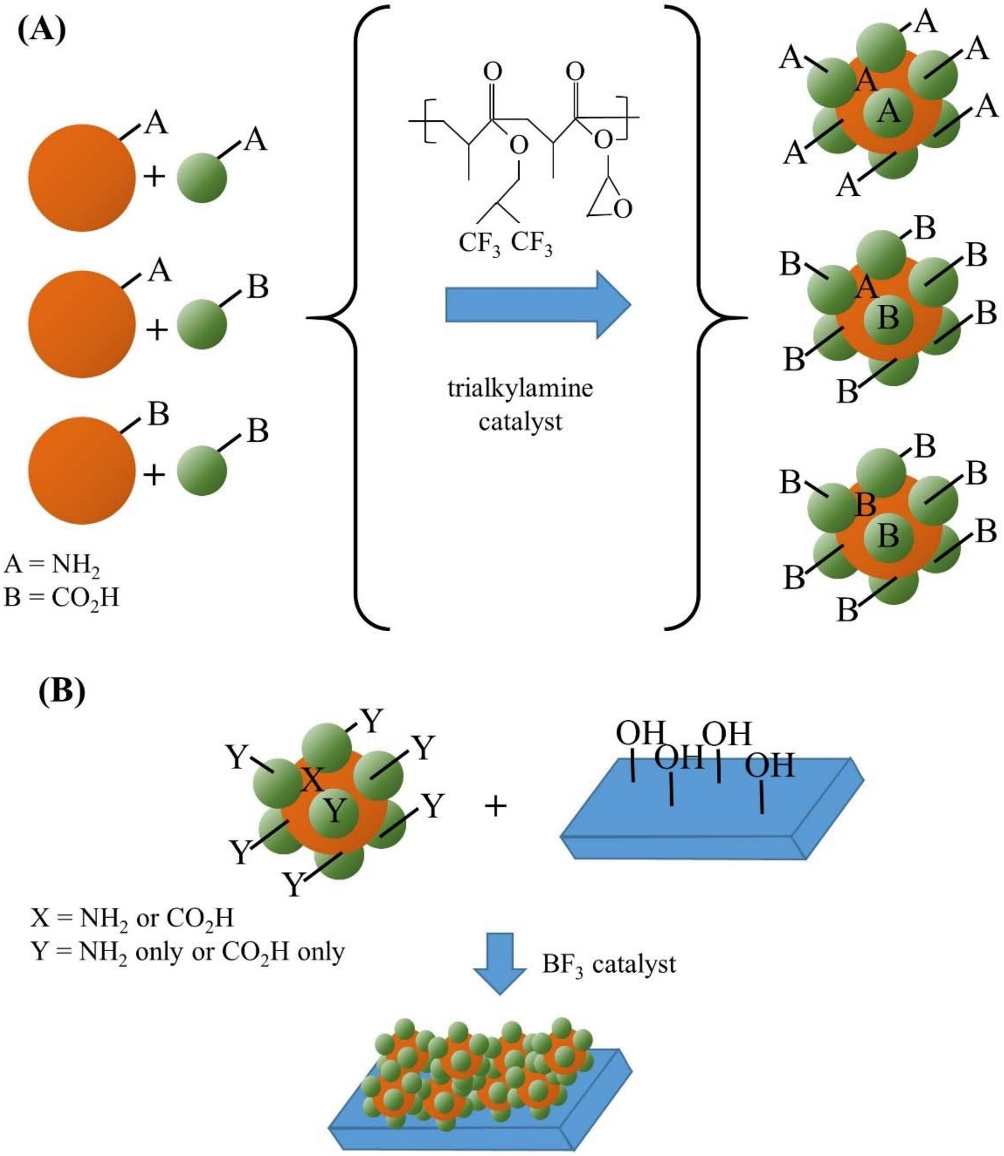


Fig. 2. (A) Use of epoxide-fluoroalkane copolymer to form raspberry-type structures and introduce a low-surface energy coating on them. The epoxide is present in the copolymer C, which also contains the fluorinated repeat unit. For clarity, attached polymer brushes are not shown. (B) Use of epoxide functionality to crosslink the raspberry-type structures to the hydroxyls present on the painted surface.

Sessile contact angles for samples evaluated under this effort used three 3 μL droplets per surface with each droplet measured independently three times for each of three targets, water, ethylene glycol, and n-heptane. Geometric surface energy was calculated based on the water and ethylene glycol interactions using software designed for the DROPimage goniometer package. Sliding angles were determined using 5 μL droplets. The droplet was applied at 0° after which the supporting platform angle was gradually increased up to 60°. Sliding angles for each of the liquids were identified as the angle for which movement of the droplet was identified. Shedding angles for each liquid were determined using 12 μL droplets initiated 2.5 cm above the coupon surface. Changes in base angle of 10° were utilized to identify the range of droplet shedding angle based on a complete lack of droplet retention by the surface (not sliding). The angle was then reduced in steps of 1° to identify the minimum required angle. Droplet diameters were determined using tools provided by Adobe Photoshop CS3. Droplets of methyl salicylate (MES; 2 μL) were applied to the surfaces and images were collected at 30 s intervals for 5 min.

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM).[2] Standard target exposures utilized a challenge level of 10 g/m^2. The painted coupons were 0.00101 m^2; the 10 g/m^2 target challenge was applied to the surfaces as two equally sized neat droplets. Following application of the target, coupons were aged 1 h prior to use of a gentle stream of air to expel target from the surface. Samples were then rinsed with soapy water (0.59 g/L Alconox in deionized water). The rinsed coupons were soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface.

For analysis of paraoxon, methyl salicylate (MES), diisopropyl fluorophosphate (DFP), and dimethyl methylphosphonate (DMMP), gas chromatography-mass spectrometry (GC-MS) was accomplished using a Shimadzu GCMS-QP2010 with AOC-20 auto-injector equipped with a Restex Rtx-5 (30 m x 0.25 mm ID x 0.25 μm df) cross bond 5% diphenyl 95% dimethyl polysiloxane column. A GC injection temperature of 200°C was used with a 1:1 split ratio at a flow rate of 3.6 mL/min at 69.4 kPa. The oven gradient ramped from 50°C (1 min hold time) to 180°C at 15°C/min and then to 300°C at 20°C/min where it was held for 5 min.

RESULTS

Initial work considered deposition of materials on glass support surfaces (Table 1). Two fluoropolymers (structures presented in Figure 3) were evaluated in combination with deposition variations. Table 1 presents the surface energy for the polyisocyante binder, the amine beads, and each of the fluoropolymers on a glass surface. Also presented are the surface energies for three raspberry coatings: coatings based on each of fluoropolymer 1 and 2 and deposited prior to the polyisocyanate cure and one based on fluoropolymer 1 deposited following the polyisocyanate cure. As expected, the raspberry coatings produce significant reduction in surface energy; however, the surfaces retain more paraoxon than the glass surface alone (Table 2). Retention of target by these glass supports (borosilicate glass coverslips) tends to be low.

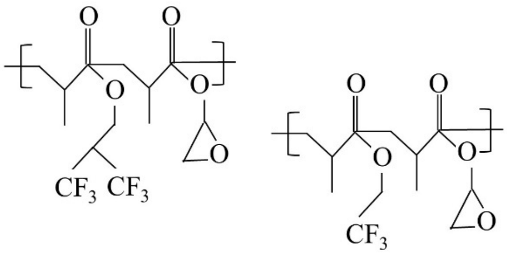


Fig. 3 — Fluoropolymers 1 (left) and 2 (right).

Table 1. Coatings on Glass Supports and Resulting Surface Energies.

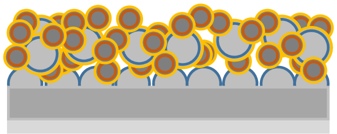
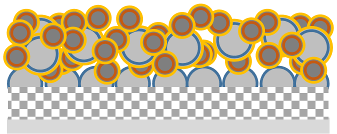
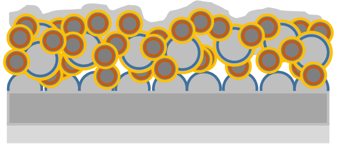
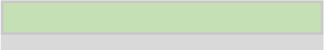
	Surface	Description	Surface Energy (mJ/m^2)
		Glass support	59.1 ± 0.2
A		Polyisocyanate on glass support	43.5 ± 0.08
B		Amine-derivatized microbeads as covalent layer on polyisocyanate	28.2 ± 0.4
C		Fluorinated raspberry clusters attached prior to polyisocyanate cure (Fluoropolymer 1)	15.9 ± 1.1
D		Fluorinated raspberry clusters attached when polyisocyanate has cured to hardness (tacky surface; Fluoropolymer 1)	11.0 ± 0.3
E		Fluorinated raspberry clusters attached prior to polyisocyanate cure with Fluoropolymer 2	14.6 ± 0.2
F		Fluoro-epoxy copolymer (1) on glass support	19.3 ± 0.03
G		Fluoro-epoxy copolymer (2) on glass support (cast from fluorinated solvent)	19.7 ± 0.05
H		Fluoro-epoxy copolymer (2) on glass support (cast from ether)	22.4 ± 0.04

Table 2 – Target Retention (g/m^2) Following 1 h Aging on Glass Supports

	Coupon	Paraoxon	DFP
Glass Support			
	Glass	0.17	
A	Polyisocyanate on glass support	0.16	0.91
B	Amine-derivatized microbeads as covalent layer on polyisocyanate	5.06	
C	Fluorinated raspberry clusters attached prior to polyisocyanate cure (Fluoropolymer 1)	0.49	1.35
D	Fluorinated raspberry clusters attached when polyisocyanate has cured to hardness (tacky surface; Fluoropolymer 1)	0.94	1.29
E	Fluorinated raspberry clusters attached prior to polyisocyanate cure with Fluoropolymer 2	1.27	
F	Fluoro-epoxy copolymer (1) on glass support	4.59	

Several variations were considered on polyurethane painted aluminum coupons. The initial approach used the fluoropolymer solution (#1 in 2.2.3.3-tetrafluoro-1-propanol) blended with the aqueous microbead solution and triethylamine catalyst. This was cast onto the painted surfaces. A control surface was also cast with using this approach with no microbeads included. The preparations used a 60 ºC overnight cure and a ratio of 1:3 beads: polymer. Variations used 5%, 10%, and 25% amine beads in the bead mixture with a total volume of 10 µL to coat a 4 cm^2 area. As shown in Table 3, these coatings produced reduced surface energy but did not result in sliding or shedding of targets at low angles. Pinning behaviors were noted. The coatings provided only modest reductions in paraoxon retention and increased DFP retention (Table 4).

Table 3 – Sessile, Sliding, and Shedding Contact Angles for Deposition Variations

Coupon	**Liquid**	**Sessile Angle**	**Sliding Angle**	**Shedding Angle**	**Geometric Surface Energy (mJ/m^2)**
Aluminum Support					
Paint Only	water	47.5 ± 1.1	>60	>60	71.9 ± 5.1
	ethylene glycol	55.7 ± 2.1	>60	>60	
	n-heptane	--	--	--	
5% amine beads with carboxylate beads (10 µL total)	water	119.2 ± 0.2	>60	>60	16.1 ± 0.8
	ethylene glycol	95.9 ± 0.6	>60	>60	
	n-heptane	--	--	--	
10% amine beads with carboxylate beads (10 µL total)	water	128.8 ± 0.3	>60	>60	17.3 ± 4.0
	ethylene glycol	102.8 ± 2.7	>60	>60	
	n-heptane	--	--	--	
25% amine beads with carboxylate beads (10 µL total)	water	116.2 ± 0.6	>60	>60	10.1 ± 1.3
	ethylene glycol	99.2 ± 1.5	>60	>60	
	n-heptane	--	--	--	
Deposition prep with no beads	water	103.5 ± 0.3	>60	>60	11.2 ± 0.3
	ethylene glycol	99.6 ± 0.4	>60	>60	
	n-heptane	--	--	--	
25% amine beads with carboxylate beads (20 µL total)	water	112.1 ± 1.4	>60	>60	9.0 ± 0.7
	ethylene glycol	98.5 ± 1.2	>60	>60	
	n-heptane	--	--	--	
25% amine beads with carboxylate beads (40 µL total)	water	110.5 ± 0.9	>60	>60	9.9 ± 0.6
	ethylene glycol	96.1 ± 0.9	>60	>60	
	n-heptane	--	--	--	
12.5% amine beads with carboxylate beads (40 µL total)	water	101.9 ± 0.9	>60	>60	11.8 ± 0.8
	ethylene glycol	97.2 ± 0.9	>60	>60	
	n-heptane	--	--	--	

Table 4 – Target Retention (g/m^2) for Deposition Variations

Coupon	**Paraoxon**	**MES**	**DFP**
Aluminum Support			
Paint Only	5.48	6.20	0.52
5% amine beads with carboxylate beads (10 µL total)	2.67		2.74
10% amine beads with carboxylate beads (10 µL total)	2.40		1.74
25% amine beads with carboxylate beads (10 µL total)	1.61		3.25
Deposition prep with no beads	3.71		2.85
25% amine beads with carboxylate beads (20 µL total)	1.86	2.96	0.94
25% amine beads with carboxylate beads (40 µL total)	1.24	1.46	1.33
12.5% amine beads with carboxylate beads (40 µL total)	1.12	1.47	1.11

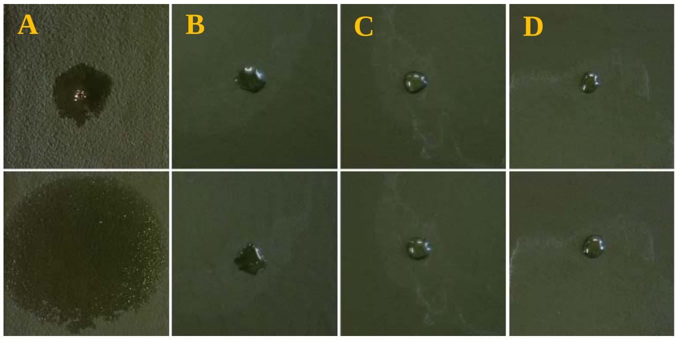


Fig. 3 — Images of a painted coupon (A) and painted coupons with different raspberry coatings immediately following application of a 2 µL droplet of MES and at 5 min following application: (B) 25% amine beads with carboxylate beads (20 µL total), (C) 25% amine beads with carboxylate beads (40 µL total), (D) 12.5% amine beads with carboxylate beads (40 µL total).

The impact of curing temperature on the resulting surfaces was considered. The differences noted for surface cured at 45 °C and 60 °C were negligible for both wetting (Table 5) and retention characteristics (Table 6). The impact of further increases in loading on the surfaces was also considered. Increasing bead loading on the surfaces required preconcentration of the commercially supplied nanoparticles. Other conditions were held constant; a curing temperature of 60 °C was used. The differences noted for surface loaded at 1:3, 1:7, and 1:9 bead: polymer were negligible (Table 7) with no surface showing significant improvements in retention behavior (Table 8). Figure 4 provides images of these deposition variations immediately following and at 5 min after application of methyl salicylate.

Table 5 – Sessile, Sliding, and Shedding Contact Angles for Curing Variations

Coupon	**Liquid**	**Sessile Angle**	**Sliding Angle**	**Shedding Angle**	**Geometric Surface Energy (mJ/m^2)**
Aluminum Support					
Paint Only	water	47.5 ± 1.1	>60	>60	71.9 ± 5.1
	ethylene glycol	55.7 ± 2.1	>60	>60	
	n-heptane	--	--	--	
12.5% amine beads with carboxylate beads (40 µL total); 60°C cure	water	101.9 ± 0.9	>60	>60	11.8 ± 0.8
	ethylene glycol	97.2 ± 0.9	>60	>60	
	n-heptane	--	--	--	
12.5% amine beads with carboxylate beads (40 µL total); 45°C cure	water	120.8 ± 0.8	>60	>60	11.3 ± 1.1
	ethylene glycol	101.3 ± 0.8	>60	>60	
	n-heptane	--	--	--	
Fluoropolymer only	water	104.5 ± 1.2	>60	>60	10.3 ± 0.5
	ethylene glycol	96.3 ± 1.1	>60	>60	
	n-heptane	19.4 ± 1.8	>60	>60	

Table 6 – Target Retention (g/m^2) for Curing Variations

Coupon	**Paraoxon**	**MES**	**DFP**
Aluminum Support			
Paint Only	5.48	6.20	0.52
12.5% amine beads with carboxylate beads (40 µL total); 60°C cure	1.12	1.47	1.11
12.5% amine beads with carboxylate beads (40 µL total); 45°C cure	0.97	4.70	0.92
Fluoropolymer only	1.57	3.89	0.55

Fig. 4 — Images of a painted coupon (A) and painted coupons with different raspberry coatings immediately following application of a 2 µL droplet of MES and at 5 min following application: (B) 12.5% amine beads with carboxylate beads (40 µL total); 60°C cure, (C) 12.5% amine beads with carboxylate beads (40 µL total); 45°C cure.

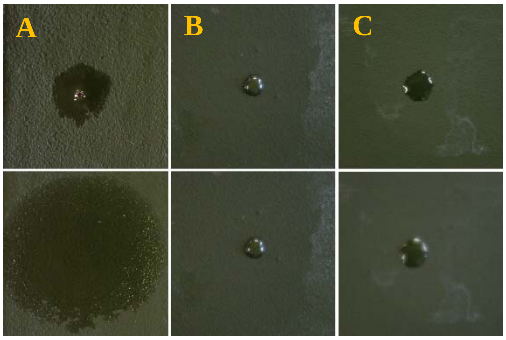


Table 7 – Sessile, Sliding, and Shedding Contact Angles for Loading Variations

Coupon	**Liquid**	**Sessile Angle**	**Sliding Angle**	**Shedding Angle**	**Geometric Surface Energy (mJ/m^2)**
Aluminum Support					
Paint Only	water	47.5 ± 1.1	>60	>60	71.9 ± 5.1
	ethylene glycol	55.7 ± 2.1	>60	>60	
	n-heptane	--	--	--	
9:1 bead: polymer	water	77.2 ± 1.7	>60	45.6 ± 1.4	29.9 ± 1.4
	ethylene glycol	58.5 ± 1.5	>60	>60	
	n-heptane	--	--	--	
7:1 bead: polymer	water	87.7 ± 3.6	>60	34.8 ± 0.8	22.3 ± 2.3
	ethylene glycol	70.2 ± 1.9	>60	>60	
	n-heptane	--	--	--	
3:1 bead: polymer	water	101.9 ± 0.9	>60	>60	11.8 ± 0.8
	ethylene glycol	97.2 ± 0.9	>60	>60	
	n-heptane	--	--	--	

Table 8 – Target Retention (g/m^2) for Loading Variations

Coupon	**Paraoxon**	**MES**	**DMMP**	**DFP**
	Aluminum Support			
Paint Only	5.48	6.20	4.28	0.52
9:1 bead: polymer	2.30	2.99	0.02	0.35
7:1 bead: polymer	1.25	1.72	0.02	0.45
3:1 bead: polymer	1.12	1.47		1.11

CONCLUSIONS

The reentrant surfaces provided by multi-sized raspberry microspheres have been described for controlled wetting and self-cleaning applications, particularly when combined with fluorinated polymers. While the materials evaluated here provide reduction in surface energy, they offer only modest differences in target retention when compared to paint only surfaces. As with many of the coatings evaluated under this effort, the coatings produce changes in the appearance of the painted coupons (Figures 3 and 4). Based on the behaviors observed for the materials considered here, no additional investigations into this type of coating will be pursued.

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