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Adhesive interactions of geckos with wet and dry fluoropolymer substrates

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Fluorinated substrates like Teflon® (poly(tetrafluoroethylene); PTFE) are well known for their role in creating non-stick surfaces. We showed previously that even geckos, which can stick to most surfaces under a wide variety of conditions, slip on PTFE. Surprisingly, however, geckos can stick reasonably well to PTFE if it is wet. In an effort to explain this effect, we have turned our attention to the role of substrate surface energy and roughness when shear adhesion occurs in media other than air. In this study, we removed the roughness component inherent to commercially available PTFE and tested geckos on relatively smooth wet and dry fluoropolymer substrates. We found that roughness had very little effect on shear adhesion in air or in water and that the level of fluorination was most important for shear adhesion, particularly in air. Surface energy calculations of the two fluorinated substrates and one control substrate using the Tabor–Winterton approximation and the Young–Dupré equation were used to determine the interfacial energy of the substrates. Using these interfacial energies we estimated the ratio of wet and dry normal adhesion for geckos clinging to the three substrates. Consistent with the results for rough PTFE, our predictions show a qualitative trend in shear adhesion based on fluorination, and the quantitative experimental differences highlight the unusually low shear adhesion of geckos on dry smooth fluorinated substrates, which is not captured by surface energy calculations. Our work has implications for bioinspired design of synthetics that can preferentially stick in water but not in air.

1. Introduction

The gecko adhesive system has fascinated many and inspired the development of hundreds of synthetic mimics. The majority of this work focuses on the dry adhesive properties of the gecko, where adhesion is driven by van der Waals forces [1]. Geckos use millions of fine hair-like structures, setae, which in many species branch and flatten into nanoscopic pads known as spatulae [2–4]. Through contact multiplication, material compliance and other factors this hierarchal system is able to increase adhesive surface area and achieve close contact with the substrate a gecko clings to [5–7]. The mechanism behind biological adhesive systems can be complex however. Specifically, when testing geckos underwater, shear adhesion no longer relies solely on van der Waals interactions, and instead also depends on the surface energy of the substrate and its interaction with water [8]; but interestingly, not the surface chemistry of the setae [9]. Other recent studies have suggested that van der Waals forces are not the primary source of adhesion and rather are also coupled with capillary adhesion, electrostatic interactions, surface charge or even nanobubbles underwater [10–15]. Thus, it is clear that the adhesive mechanism of a biological adhesive system like the gecko's may be complicated for free-ranging geckos in complex natural environments.

One particularly interesting class of surfaces in gecko adhesion and gecko-inspired adhesion are fluorinated surfaces. These 'non-stick' surfaces,

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like commercially available poly(tetrafluoroethylene) (PTFE), have been known to foil the gecko's incredible adhesive system, rendering them virtually dysfunctional (i.e. unable to support their body weight) [8,16,17]. While not many studies have investigated adhesion to wet fluorinated surfaces, the results are intriguing. For example, when testing gecko-inspired PTFE pillars, underwater adhesion was 70% of adhesion in air [18]. Yet when testing live geckos on PTFE, shear adhesion is very low in air but substantial in water (ratio of wet to dry adhesion is 5.19) [8]. The enhancement of whole-animal shear adhesion underwater was particularly surprising considering the very low shear adhesion values in air on PTFE (1.6 N in air versus 8 N in water). Furthermore, theoretical models based on surface energy calculations correctly described whole-animal shear adhesion in air and in water for various other substrates (glass, poly(methylmethacrylate) (PMMA) and glass coated with a hydrophobic self-assembled monolayer) but not PTFE. These models assumed, however, that each surface was structurally homogeneous (i.e. smooth), which is certainly not the case with PTFE. Thus there may be other factors, specifically roughness, influencing gecko shear adhesion to submerged PTFE, rendering work of adhesion models based on smooth surfaces insufficient.

In an effort to clarify the effect of fluorination and roughness on adhesion to wet and dry substrates, we tested geckos on relatively smooth substrates with differing degrees of fluorination and compared these results with a relatively smooth non-fluorinated control substrate. We hypothesized that shear adhesion to the fluorinated substrates will be higher underwater than in air, similar to previous results [8]. We also expected that these substrates would have higher shear adhesion in air and in water than previous results on PTFE because of the reduction of roughness in this study [19–23]. Our second hypothesis was that shear adhesion will vary based on the degree of fluorination, where a fully fluorinated substrate (perfluorinated, such as fluorinated ethylene propylene (FEP)) will have lower shear adhesion values in air and in water than a partially fluorinated substrate (such as ethylene tetrafluoroethylene (ETFE)) [24,25]. Likewise, we hypothesized that our control, non-fluorinated substrate, will have no difference in shear adhesion in water and in air, corresponding to our previous results on hydrophobic, non-fluorinated substrates. Finally, our third hypothesis relates to theoretical calculations of the work of adhesion in air and water on each of our substrates. By calculating the surface energy of these substrates using a Tabor–Winterton approximation (TWA) and using relatively smooth fluorinated substrates we will be more accurate at predicting adhesion to wet and dry substrates, similar to Stark *et al.* [8] and Badge *et al.* [9]. Our results here have implications not only for gecko adhesion and gecko-inspired synthetics but also for fundamental adhesion properties of fluorinated substrates.

2. Material and methods

2.1. Experimental procedure

2.1.1. Surface characterization

Two fluoropolymer substrates, FEP and ETFE, were used in experimental trials and theoretical calculations. Polyethylene terephthalate (PET) was used as a control, non-fluorinated substrate. Substrates were obtained from DuPont (DuPont™ Tefzel® ETFE FluoroPLASTIC FILM, Properties Bulletin K-26943 1, October 2013 and DuPont™ Teflon® FEP FLUOROPLASTIC FILM, Properties Bulletin K-26941, May 2013). Atomic force microscopy (Dimension ICON, Veeco) in tapping mode at 0.5 Hz was used to characterize the roughness of each of these substrates as well as a PTFE substrate tested previously [8] and used here as a comparison (see Discussion). Contact angle measurements were done on each substrate as described below.

2.1.2. Whole-animal adhesion

Six Tokay geckos (*Gekko gecko*) (average weight of 103.4 ± 4.3 g) were used for experimental trials. Geckos used for experiments were housed individually and husbandry schedules followed as outlined by Niewiarowski *et al.* [26]. Prior to experiments, geckos were introduced to a walk-in environmentally controlled chamber that was kept at 24.5 ± 0.1°C and 33.4 ± 0.3% relative humidity for all experiments. The geckos were allowed a 30 min time period to acclimate to the testing environment. Three substrates (FEP, ETFE and PET) were used in the whole-animal experiment. These thin substrates were fastened to acrylic plates to provide support, which were in turn mounted to a Rubbermaid container which was used to hold water during trials [27]. Geckos were fitted with two harnesses around their pelvis that were attached to a horizontally positioned force sensor on a motorized track, similar to the set-up used by Niewiarowski *et al.* [26] and Stark *et al.* [27] (electronic supplementary material, figure S1). Maximum shear adhesive force was defined as the point at which all four feet began to slip along the substrate (shear adhesion) (electronic supplementary material, figure S2). In the wet substrate condition, the substrate was fully submerged in water (22.4 ± 0.2°C) to a depth of approximately 1 cm, completely covering the gecko's feet. Substrates were cleaned with ethanol and then water after each test in air. Substrates submerged in water were cleaned after all six animals had been tested. Geckos were tested randomly on all substrates and in both wet and dry conditions.

Only the maximum shear adhesive force recorded from three trials per individual, substrate and treatment were used in the statistical analysis. The effect of substrate type (FEP, ETFE or PET) and treatment (air or water) on shear adhesion was tested using a repeated-measures mixed model where treatment, substrate and their interaction (treatment × substrate) were the fixed effects and the identification code of the individual geckos was the random effect (JMP® 11 Documentation Library, SAS Institute Inc., Cary, NC, USA). A matched pairs analysis was used to compare specific treatments of interest, such as shear adhesion in air and in water on each substrate [8]. Means are reported as mean ± 1 s.e.m.

2.1.3. Theoretical modelling procedures

Taking into account a simple system (two flat surfaces), we calculated the work of adhesion in a system consisting of a substrate s, gecko foot g and medium (e.g. air or water) m. The work of adhesion is the difference between the energy required to make a new interface between the substrate and gecko foot, γ_{sg}, and the energy recovered from the elimination of the two interfaces of gecko foot and substrate with the medium, γ_{gm} and γ_{sm}, respectively. The work of adhesion for separating two flat surfaces is therefore given by [28–30]

$$W = \gamma_{gm} + \gamma_{sm} - \gamma_{sg}. \tag{2.1}$$

A positive value of W indicates that the adhesion process is energetically favourable. The use of adhesion in this model refers to adhesion energy per unit area required to separate the two surfaces in the normal direction. In addition, this equation assumes that the contact underwater is dry.

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The surface free energy γ of a material may be described as the sum of its polar and non-polar contributions: $\gamma = \gamma^{(p)} + \gamma^{(np)}$. The non-polar contribution arises primarily from van der Waals–London dispersion (vdW-Ld) forces [29] while the polar contribution arises from both permanent dipoles in the material, as well as mobile charges that may migrate to the interface. While the interfacial energy γ_{sm} may be determined readily from contact angle measurements, experimental complications preclude the direct determination of γ_{gm} or γ_{sg} by this method. However, because the indices of refraction are well defined for all relevant materials, the non-polar contributions $\gamma_{gm}^{(np)}$ and $\gamma_{gs}^{(np)}$ may be estimated via the TWA. The polar component of the interfacial energy was calculated using the Wu approach [31,32] by measuring the water contact angle and using Young's equation to calculate the interfacial energy of the substrate in contact with water. This combined approach is labelled TWA-CA in the rest of the paper.

Using values from the TWA-CA, we can also then model a complex system more representative of the fibrillar adhesive system of the gecko. In this model we use a structured unit cell of four square pillars 4 µm wide, 60 µm tall and spaced 1 µm apart (see Stark *et al.* [8] for details; electronic supplementary material, figure S3*a*). This structure takes into account the dimensions of setae and also allows us to factor into the work of adhesion (W) the exclusion of water between the pillars both prior to contact and during contact, as was confirmed by visual observations of the gecko toe (see Stark *et al.* [8] for details; electronic supplementary material, figure 3*b*). The actual geometry of gecko setae is of course more complicated, and has been modelled before [33], however in this context, the patterned unit cell surface yields similar results to a flat surface model (Stark *et al.* [8]). In these calculations, we compare the work of adhesion in water (W_{wet}) with the work of adhesion in air (W_{dry}) using a ratio ($W_{wet} : W_{dry}$). A ratio is used as these values are not without major assumptions, and instead we are estimating the magnitude and direction of adhesion in air and water and comparing that with experimental measurements of the live geckos. Specifically, model calculations assume normal adhesion, rather than shear adhesion like the whole-animal experiments, and they assume a dry, homogeneous contact both chemically and structurally (i.e. capillary adhesion is not allowed). Modelling was done in the normal adhesion geometry, rather than shear adhesion (vertical versus lateral), which are proportional [34]. Additionally, unlike our previous work, experimental results can be compared more readily with the theoretical results, as experimental substrates do not have the high roughness level of PTFE, which could not be accounted for in the theoretical calculations from previous work [8].

Lastly, in addition to the calculations of the ratio ($W_{wet} : W_{dry}$) using the TWA-CA approximation and the model gecko unit cell, we have also calculated this ratio assuming that the setae are coated with an oil-like material (modelled as *n*-hexadecane). This assumption is based on the discovery of lipid material at the contact interface between the gecko toe and substrate, along with lipid footprints left behind geckos as they walk [35]. This assumption has been used previously to model the gecko unit cell and PTFE [8], however again, the surface roughness of PTFE was not accounted for in the model and may be why the theoretical predictions do not match the experimental results. The use of relatively smooth fluorinated substrates here removes this unaccounted source of error in our predictions.

We present the theoretical model we have used to calculate the surface and interfacial energies in §1. Because the van der Waals interactions only capture the non-polar interactions, we have used the Wu method to determine the polar component of the surface and interfacial energies in §2 [31,32]. In §3, we discuss the setae geometry and equation we use for calculating the $W_{wet} : W_{dry}$ ratio both using the TWA-CA and the oil-like material coating. Our goal is to investigate the use of the structured TWA-CA model and the oil-like material coating the structured model on predicting the experimental results on all three substrates.

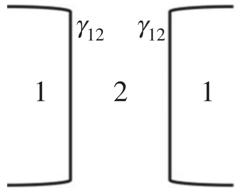

Figure 1. Diagram of a three-layer (121) system consisting of two semi-infinite half-spaces of material 1 separated by an interlayer medium 2. The interfacial energy at each interface is given by γ_{12}.

1. Non-polar contribution: surface energy estimation using van der Waals–London dispersion forces

The non-polar vdW-Ld contribution to the interfacial free energy is equivalent to half the free energy of the interaction between two identical blocks of non-polar material 1 in medium 2, denoted as E_{121} (figure 1), and is therefore given as

$$\gamma^{(np)} = \frac{1}{2}E_{121} = \frac{A_{121}}{24\pi d_0^2}, \qquad (2.2)$$

where A_{121} is the Hamaker coefficient [36] for two blocks of material 1 separated by medium 2, and d_0 is the interlayer separation, generally taken as 0.165 nm [29].

The Hamaker coefficients were estimated using the TWA [29,37] in which the visible-range index of refraction n_i of each material i is taken as a proxy for the vdW-Ld interaction strength of each material. TWA gives the Hamaker coefficient as

$$A_{121}^{TWA} = \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^2 + \frac{3\pi\hbar\nu_e}{8\sqrt{2}}\frac{(n_1 - n_2)^2}{(n_1 - n_2)^{3/2}}, \qquad (2.3)$$

where k is the Boltzmann constant, T is the system temperature, ε_i is the dielectric constant for a material i (given by the relation $\varepsilon = n^2$), $\hbar$ is Planck's constant divided by 2π and ν_e is the electronic absorption frequency, generally taken as $3 \times 10^{15}\ s^{-1}$. This approximation neglects the details of the UV absorptions of the materials, which may be non-trivial [38], but for comparisons between similar materials such as those included in this study, provides a reasonable prediction of trends and relative interaction strengths. Hamaker coefficients, A_{121}^{TWA}, were calculated using literature values for the indices of refraction (table 1). The interfacial energy between two dissimilar materials was calculated using the index of refraction of one material for the isotropic blocks, and the index of refraction of the second for the medium [29,42].

2. Polar contribution: surface contact angle measurements using Wu method

To take into account polar interactions, static contact angle measurements were taken on FEP, ETFE and PET using a Krüss DSA25 Drop Shape Analyzer (KRÜSS GmbH, Hamburg, Germany). Measurements were taken for contact angles of both water and diiodomethane (2–3 µl), and both polar and dispersive free energy were calculated using the Wu method [31,32]. Substrate–water interfacial energies were subsequently calculated using the Young equation [30]:

$$\gamma_{sl} = \gamma_s - \gamma_l\cos(\theta), \qquad (2.4)$$

where θ is the contact angle of water on the substrate and γ_l is the interfacial tension of water, taken as 72.8 mJ m^{-2} [43].

3. Modelling with complex geometry

In these calculations, we have modelled a unit cell of four-square pillars with the dimensions of a Tokay gecko (*Gekko gecko*) setae. The model represents the state where water does not penetrate the columns both prior to and during contact

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Table 1. Visible-range (approx. 600 nm) indices of refraction for materials included in this study [39–41] (also see DuPont™ Tefzel® ETFE FluoroPLASTIC FILM, Properties Bulletin K-26943 1, October 2013 and DuPont™ Teflon® FEP FLUOROPLASTIC FILM, Properties Bulletin K-26941, May 2013).

material	n_{vis}
FEP	1.34
ETFE	1.40
PET	1.58
water	1.33
air	1.00
β-keratin	1.55

with the substrate. We included the air–water surface tension term to account for air trapped between the setal structures in our model unit cell. This is slightly different than the calculations from Stark *et al.* [8] and is explained further by Badge *et al.* [9]. Taking into account these assumptions, the ratio of the work of adhesion in water and the work of adhesion in air ($W_{wet}:W_{dry}$) of a structured surface is

$$\frac{W_{wet}}{W_{dry}} = \frac{\gamma_{g\text{-water}} - \gamma_{g\text{-s}} + \gamma_{s\text{-water}}\, a_2/a_C + \gamma_{water\text{-air}}(a_2/a_C - 1) - \gamma_{s\text{-air}}(a_2/a_C - 1)}{(\gamma_{g\text{-air}} + \gamma_{s\text{-air}} - \gamma_{g\text{-s}})}, \tag{2.5}$$

where $\gamma_{g\text{-water}}$ is the interfacial energy of the gecko surface and water, $\gamma_{g\text{-air}}$ is the interfacial energy of the gecko surface and air, $\gamma_{water\text{-air}}$ is the air–water surface tension term, $\gamma_{s\text{-air}}$ is the surface energy of the solid surface, $\gamma_{s\text{-water}}$ is the interfacial energy of solid in contact with water, $\gamma_{g\text{-s}}$ is the interfacial energy of gecko in contact with solid surface, a_2 is the surface area of the unit cell (121 μm^2) and a_C is the area of contact (64 μm^2). This ratio can be calculated using the surface and interfacial energies described in §§1 and 2.

We have also directly calculated the $W_{wet}:W_{dry}$ ratio using contact angle measurements of hexadecane and water on these smooth substrates. In this case, we have approximated the gecko surface to be similar to that of hexadecane liquid (h). Based on this assumption, the ratio of $W_{wet}:W_{dry}$ is

$$\frac{W_{wet}}{W_{dry}} = \frac{\gamma_{h\text{-water}} + \gamma_{h\text{-air}}\cos\theta_{h\text{-s}} + \gamma_{water\text{-air}}[(a_2/a_C)(1-\cos\theta_{s\text{-water}}) - 1]}{\gamma_{h\text{-air}}(1+\cos\theta_{h-s})}. \tag{2.6}$$

Theta values, $\theta_{h\text{-s}}$ and $\theta_{s\text{-water}}$ were measured for each substrate at the completion of whole-animal tests using Ramé-Hart Instruments Advanced Goniometer 500 F1 with Drop Image Advanced software (table 2).

3. Results

3.1. Whole-animal adhesion

When testing for the effect of substrate (FEP, ETFE or PET) and treatment (air or water) on shear adhesion, we found that shear adhesion was significantly affected by substrate ($F = 18.8489$, d.f. = 2, $p < 0.0001$) and by the interaction of substrate and treatment ($F = 6.4453$, d.f. = 2, $p = 0.0055$) (table 3). Specifically, we found that shear adhesion on FEP was significantly higher in water than air (6.44 ± 0.99 N in water, 0.74 ± 0.12 N in air; $t = 5.99$, d.f. = 5, $p = 0.0019$).

Table 2. Contact angle measurements for the work of adhesion of a structured surface (§3) where the gecko surface is assumed to be similar to *n*-hexadecane. Error bars are mean ± 1 s.d.

	water (°)	*n*-hexadecane (°)
FEP	110.7 ± 0.6	50.9 ± 1.9
ETFE	100.0 ± 4.0	44.5 ± 1.6
PET	76.0 ± 1.0	complete wetting

This was also the case on ETFE (8.46 ± 0.80 N in water, 2.53 ± 0.76 N in air; $t = 10.34$, d.f. = 5, $p = 0.0001$). Conversely, shear adhesion on PET was not different in air or water (11.88 ± 3.94 N in water, 18.86 ± 3.42 N in air; $t = -1.40$, d.f. = 5, $p = 0.2214$) (figure 2).

3.2. Theoretical calculations

Hamaker coefficients and interfacial and surface free energies from TWA, along with polar, non-polar and total surface free energy from contact angle measurements, are presented in table 4. TWA makes accurate predictions of total surface energies for highly non-polar systems, such as gecko skin, which consists of a relatively non-polar protein, β-keratin, coated with a highly non-polar *n*-hexadecane-like monolayer [8,35,44]. Therefore, the value of the gecko foot–air interface given by TWA, γ_{ga}^{TWA}, may be assumed to be relatively accurate, as are the values of γ_{gs}^{TWA} given the mostly non-polar nature of their surface energies. Because $\gamma_w = 72.8$ mJ m^{-2} and the contact angle of water on gecko skin is $\theta = 90°$ [9,45], the Young equation may be readily employed to predict the value of the gecko foot–water interfacial energy $\gamma_{gw} = 40.2$ mJ m^{-2}. The ratio of $W_{wet}:W_{dry}$ calculated using the TWA-CA method to model the structured gecko surface (equation (2.5)) and hexadecane to model the structured gecko surface (equation (2.6)) are shown in table 5.

In relation to whole-animal experimental trials, we find a similar trend in the theoretical calculation of the work of normal adhesion and the experimental ratio of shear adhesion measured for geckos on PET, ETFE and FEP substrates. In these calculations the two fluorinated substrates, FEP and ETFE, have $W_{wet}:W_{dry}$ ratios which favour adhesion on wet substrates. Interestingly, PET has a $W_{wet}:W_{dry}$ ratio of 0.6 in whole-animal trials, much less than theoretical predictions (table 5). It is possible that this discrepancy is related to water between the adhesive toe pad and the PET substrate during experimental trials, a condition that is not allowed in theoretical models. Finally, the general trend is the same, where $W_{wet}:W_{dry}$ ratios are highest for the fully fluorinated substrate FEP, lowest for the non-fluorinated PET and intermediate for the partially fluorinated ETFE.

4. Discussion

Gecko-inspired synthetic designs have primarily been focused on building structures that resemble the geometry of the gecko adhesive system. This focus has been quite successful. In recent studies, however, the role of substrate and surface chemistry on gecko adhesion in the presence of water has been investigated, and the results are not yet clear [8,9,14,46,47]. We argue that turning our attention to these aspects is likely to improve design and performance

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Table 3. The repeated-measures fixed effect table shows a significant difference in shear adhesion across substrate (ETFE, FEP and PET) and the interaction of substrate and treatment (air or water). The asterisk denotes statistical significance ($p \le 0.05$). The significant interaction shown below arises from substrate, specifically the lack of statistical significance between shear adhesion in air and water on PET.

effect	d.f.	d.f. denominator	*F* ratio	*p*-value
treatment	1	25	0.8484	0.3658
substrate	2	25	18.8489	<0.0001*
substrate × treatment	2	25	6.4453	0.0055*

Table 4. Hamaker coefficients and surface free energies from TWA for all relevant materials systems, as well as polar, non-polar and total surface free energies from experimental contact angle measurements.

			surface free energy from contact angle measurements		
materials	Hamaker coefficient from TWA A_{121} (zJ)	surface free energy from TWA $\gamma^{(np)}$ (mJ m^{-2})	$\gamma^{(np)}$ (mJ m^{-2})	$\gamma^{(p)}$ (mJ m^{-2})	$\gamma^{(total)}$ (mJ m^{-2})
PET–water	15.8	7.7	—	—	37.2
PET–air	90.3	44.0	45.3	9.3	54.6
ETFE–water	1.3	0.7	—	—	42.8
ETFE–air	47.7	23.2	26.5	3.2	29.7
FEP–water	0.03	0.01	—	—	46.0
FEP–air	35.7	17.4	18.3	1.9	20.2
gecko–water	12.4	6.1	—	—	—
gecko–air	82.6	40.2	—	—	—
PET–gecko	0.2	0.1	—	—	—
ETFE–gecko	5.7	2.8	—	—	—
FEP–gecko	11.3	5.5	—	—	—

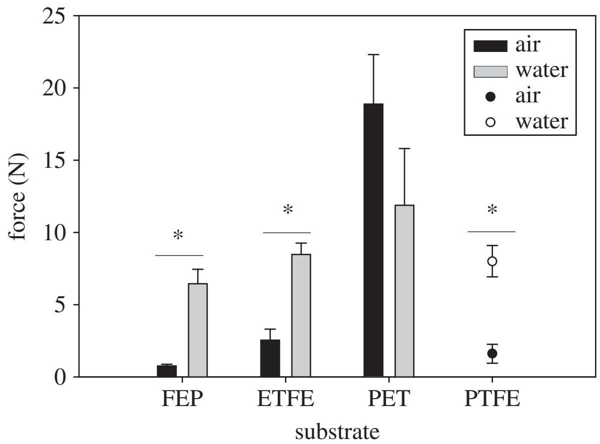

Figure 2. Bars represent average maximum shear adhesion in air (black bars) and water (grey bars) on three substrates (FEP, ETFE and PET). Prior results on PTFE are included for comparison (black and white points). Error bars are mean ± 1 s.e.m. The asterisk denotes significant statistical difference ($p \le 0.05$) between the treatment groups (air and water).

Table 5. $W_{wet}:W_{dry}$ ratios of each of the theoretical calculations: the estimates using structured geometry and the TWA-CA approximations, estimates using structured geometry and *n*-hexadecane, and finally the experimental ratios from whole-animal shear adhesion.

	$W_{wet}:W_{dry}$		
	FEP	ETFE	PET
theoretical (structured using TWA-CA)	3.1	2.3	1.33
theoretical (structured using *n*-hexadecane)	4.3	3.6	2.1
experimental	8.7	3.3	0.6

of biomimetic synthetics. Indeed, the current state of the art in gecko-inspired adhesives still does not fully capture the performance capabilities of the natural system [48]. In fact, our best synthetics outperform geckos in only a single dimension, adhesive strength [49,50]. In this study, we took a detailed investigation of one type of substrate that has presented particularly intriguing results: fluorinated substrates. In whole-animal shear adhesion trials, geckos were unable to hold their body weight on dry PTFE [8]. This phenomenon has been documented previously [16,17]. Surprisingly, however, when submerged underwater geckos adhered to wet PTFE much stronger than dry, by a factor of four [8]. This behaviour was not replicated in smooth, non-fluorinated hydrophobic substrates [8]. PTFE, however, is a manufactured material that is quite rough, calling into

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question the role of air pockets and capillary adhesion when submerged. To remove this additional factor we tested geckos on relatively smooth fluorinated and non-fluorinated substrates in both air and water. Similar to results on wet PTFE, we found that geckos adhered to the smooth fluorinated substrates better in water than in air. Conversely, there was no difference in shear adhesion in air or water on the control substrate, which was intermediately wetting ($\theta \sim 90^{\circ}$). Theoretical model calculations support these results but clearly point to additional factors that are not captured in the model calculations.

Although we do not expect geckos to encounter fluorinated substrates in their natural environment, the previous results on rough PTFE raise an important question: what is the role of roughness on wet substrates? Gecko adhesion to rough substrates has been tested previously at a variety of size scales and substrates [19–23]. Generally, adhesion seems to be reduced on rough surfaces, especially those that scale on the size of the adhesive components, specifically the spatula (nanometre) and lamellae (millimetre) [19,20], though this is also likely for the setae (micrometre) [21] and also toe pad (centimetre). The substrates used in this experiment were relatively smooth, root mean square (RMS) roughness was between 4 and 42 nm on all three substrates (FEP ~ 40 nm; ETFE ~ 20 nm; PET ~ 4 nm; electronic supplementary material, figure S4). This is in contrast to PTFE, which had a RMS roughness of approximately 230 nm (electronic supplementary material, figure S4*d*). Interestingly, surface roughness of PTFE is directly at the scale of the spatula (approx. 200 nm wide), thus this should be one of the most difficult asperity sizes for geckos to cling to [20]. As such we would expect values for the relatively smooth fluorinated substrates, FEP and ETFE, to be much higher than PTFE, simply based on this principle alone. This was not the case however. Shear adhesion to FEP and ETFE was not qualitatively higher than shear adhesion to PTFE in air (figure 2), suggesting that roughness is not the most limiting factor in shear adhesion to fluorinated substrates in air. This is a bit surprising and counter to our hypothesis, as roughness at this scale has been demonstrated to be a major limitation for adhesion [20]. Interestingly, in water the effect of roughness again seems to be minimal. Shear adhesion in water on the two relatively smooth fluorinated substrates does not qualitatively differ from shear adhesion to wet PTFE in previous work. Thus, roughness has very little effect on shear adhesion in air or in water on fluorinated substrates.

While wet fluorinated substrates do not exist in the gecko's native environment, wet rough hydrophobic substrates are probably common. For example, many plant surfaces, especially leaves, are rough at multiple length scales [51] that correspond to several hierarchically structured components of the gecko adhesive system. Roughness produced by self-assembling waxes (tens to hundreds of nanometres) on the surfaces of variously shaped epidermal cells (micrometres) provide the chemical and physical basis for leaf hydrophobicity including the lotus and salvinia effect [52]. In fact, the ubiquity of variably rough surfaces at what should be challenging length scales for the gecko system [19] highlight significant gaps in our understanding of how geckos are so adept at moving through their three-dimensional habitats with such ease. Our work suggests that geckos may be able to adhere to wet rough substrates as well as they adhere to wet smooth substrates. As others have suggested [53], more empirical and theoretical work with physico-chemical determinants of how surfaces interact with water will probably be required to separate the role of fluorination in shear adhesion to the substrates tested here, and to explain how geckos successfully adhere to the vast array of surfaces they encounter in nature.

In addition to controlling for the effect of roughness on shear adhesion to wet fluorinated substrates, we were also interested in investigating the consequence of degree of fluorination on shear adhesion in air and water. We hypothesized that there would be a gradient of shear adhesion based on degree of fluorination, where FEP would have lower shear adhesion in air and water than ETFE, which in turn would be lower than the non-fluorinated control PET. In air the effect of fluorination was very clear and as expected. Dry FEP had very low shear adhesion values (0.74 ± 0.12 N) and ETFE was just nearly significantly higher (2.53 ± 0.76 N; $t = -2.54$, d.f. $= 5$, $p = 0.0519$). Shear adhesion to dry PET was high (18.87 ± 3.42 N) and in the range of previous results on non-fluorinated dry substrates such as dry glass, dry PMMA and dry glass coated with a hydrophobic self-assembled monolayer (OTS-SAM) [8]. In water there was no such trend. Instead, shear adhesion to wet FEP and wet ETFE was no different in whole-animal tests ($t = -1.87$, d.f. $= 5$, $p = 0.1208$). Interestingly, PET was also lower than expected (11.88 ± 3.94 N) when compared with a material with a similar water contact angle (PMMA wet shear adhesion $= 24.0 \pm 3.92$ N), though like other non-fluorinated intermediately wetting and hydrophobic substrates, PET did not differ in shear adhesion across treatment (air or water) [8]. Overall, these results only partially support our hypothesis and suggest that although fluorination is key to enhanced shear adhesion underwater, the degree of fluorination is relatively trivial in water but not in air.

Although our models support the experimental results in two ways: (i) shear adhesion in water is higher than air and (ii) there is a consistent qualitative trend in $W_{wet}:W_{dry}$, where FEP > ETFE > PET across models, our theoretical models still do not predict the magnitude of the experimental results. For instance, in the case of the fully fluorinated FEP, gecko shear adhesion in water was much higher than air (experimental $W_{wet}:W_{dry} = 8.7$), however, neither of the three models fully predicts the level of this magnitude (table 5). Although it is easy to focus on the improved adhesion in water which leads to an imbalance of ratios in both the theoretical and experimental results, it is also important to recognize the very poor adhesion in air measured in experimental trials. For example, setting PET to 1, we get W_{dry} for the three substrates in experimental trials as 1.0 : 0.13 : 0.04 (PET : ETFE : FEP). However, when using the theoretical model for the structured surface approximated by the TWA-CA, W_{dry} is 1.0 : 0.72 : 0.62 (PET : ETFE : FEP). Based on theory, W_{dry} is only expected to reduce by 28–38% for fluorinated surfaces compared with the ratio measured for PET. Instead, the experimental values for shear adhesion on dry fluorinated surfaces are much lower (87–94%), which explains why the ratios of W_{wet}/W_{dry} are much higher for fluorinated surfaces compared with hydrocarbon surfaces. Further work is required to assess the specific contributions of normal and shear on adhesion to fluorinated substrates tested in air and water.

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Our results raise several interesting points. First, the nanometre-sized roughness of the PTFE sheet tested earlier has little effect on shear adhesion in air or water when compared with the relatively smooth fluorinated substrates tested here, and rather, it appears that the degree of fluorination is key to the low shear adhesion values in air. The degree of fluorination does not seem to have an effect on shear adhesion in water, however. Second, theoretical models support the general trend in wet and dry adhesion across substrates but do not predict the magnitude of difference between wet and dry adhesion. These models bear specific limitations, such as adhesion geometry, that if elucidated could help us understand not only gecko adhesion on fluorinated substrates but basic adhesion principles of fluorinated substrates in air and water. Additionally, the interaction of substrate and medium (air or water) is particularly highlighted in this study. Without improving our understanding of how two surfaces interact with one another in air and water, we will not be able to accurately predict adhesion behaviour in more complex media and with varying substrates. Finally, although geckos do not encounter fluorinated substrates in their natural environment, the mechanism in which the van der Waals-based adhesive system improves adhesion underwater compared with the 'non-stick' behaviour in air has interesting application potential for synthetic adhesives that are tuned to wet environments and can be easily removed, or even self-detach when transitioned to a dry environment.

Ethics. All procedures using live animals were approved by the University of Akron IACUC protocol 07–4G and are consistent with guidelines published by the Society for the Study of Amphibians and Reptiles (SSAR 2004).

Data accessibility. The datasets supporting this article have been uploaded as part of the electronic supplementary material.

Authors' contributions. A.Y.S. and J.O. carried out the whole-animal adhesion experiments. D.M.D. and K.A.P. carried out the TWA-CA measurements and calculations. A.D. and A.Y.S. calculated the gecko model in Material and methods section §2.1.3. A.Y.S., D.M.D., P.H.N., R.H.F. and A.D. conceived and designed the project. A.Y.S., D.M.D., J.O., P.H.N. and A.D. wrote the manuscript. All authors gave final approval for publication.

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