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Article

Snail Deterrent Properties of a Soot Based Flexible Superhydrophobic Surface

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Received: 7 March 2014 / Accepted: 17 May 2014 / Published: 26 May 2014

Abstract: Snails enjoying eating the leaves of many garden plants. Deterring this pest without resorting to chemicals can present a significant challenge. A previous report (PLoS ONE 7(5): e36983) suggested that loose soot was a surface to which snails found adhesion difficult. Soot may also be embedded into a PDMS substrate making a flexible membrane with superhydrophobic properties (Appl. Phys. Lett. 102 (21) 214104). In this article we investigate whether the embedded soot has the same anti-adhesive properties to snails as the loose soot, so giving the possibility of a facile method for protecting crops from this pest. Data is presented showing the force required to remove snails from the soot/PDMS surfaces using a simple spinning technique. The receding contact angles have also been measured for various concentrations of an anionic surfactant on the soot/PDMS surface and compared to the data presented in the PLoS ONE article. In addition, simple time lapse video demonstrations are presented that show the reluctance of the snails to move over the soot based surfaces suggesting that the soot/PDMS structure does indeed provide a level of deterrence to this garden pest.

Keywords: superhydrophobic; snail; contact angle; anti-adhesive; soot;

1. Introduction

Snails move using a process called adhesive locomotion by producing a thin layer of mucus and using its non-linear properties to create a pedal wave. Adhesive locomotion is one of the most effective but energetically expensive methods of locomotion known in biology [1]. The snails have a single foot and the mucus acts both as an adhesive and in propulsion. Pedal mucus, which has 91% to 98% of its content as water, has mechanical properties dependent on how fast the material is deformed [2]. Recent work has used rheometers to assess the properties of snail mucus and attempted to find substances that mimic the same properties [3]. With such high water content, it may seem appropriate to consider the very water repellant properties of superhydrophobic surfaces [4] as possible repelling surfaces for snails. Superhydrophobicity occurs when a chemically hydrophobic surface also has high aspect ratio surface roughness or texture [5]. Using a range of commercially available superhydrophobic coating, Shirtcliffe et al [6] investigated the ability of such coatings to repel snails. One result that did not receive much comment in that article was the data showing that loose soot provided one of the most snail resistant surfaces; the durability of loose soot making it impractical as a snail deterrent. In this work we look at the snail deterrent properties of a novel type of superhydrophobic surface produced by embedding the soot from burning rapeseed oil in a PDMS substrate, thus making a flexible membrane with superhydrophobic properties; a type of surface which has recently been reported for use in Capillary Origami [7].

2. Results and Discussion

In figure 1 we show some simple tests that demonstrate the reluctance of snails to cross the soot/PDMS surfaces. Figure 1a shows a simple acrylic zigzag track bounded by soot/PDMS, mounted vertically with some snail food at the top. The figure shows a sequence of overlaid images taken as a snail ascends up the track. Figure 1b shows two polypropylene containers, one with a soot/PDMS coating and one without any coating, both with snail food on top. Snails were admitted to the enclosure and the containers were photographed again after 24 hours (figure 1c). None of the food on the soot/PDMS coated container was consumed after 24 hours, although eventually after 2 days one snail climbed the soot. These simple tests show that a soot/PDMS coating has deterrent properties to snails.

Shirtcliffe et al [6] used a technique to spin snails adhering to a horizontal surface to find the speed at which they were removed and from this calculated the force for removal using an average snail mass. Our spinning technique was identical however we also recorded the foot area for the young snails as they grew. This is shown in figure 2 and provides a strong linear relationship between footprint area and mass of snail. This enabled the removal force per unit area of footprint to be estimated for a range of surfaces and these are shown in figure 3. This may be a more informative measure than the simple '*g*' value used by Shirtcliffe et al [6]. To allow comparison between the two data sets, we measured a number of standard surfaces that they also reported (glass, loose soot and acrylic). As with the Shirtcliffe et al data, the loose soot was found to require the least force to remove the snails (figure 3) closely followed by the unrinsed soot/PDMS surface and then the rinsed soot/PDMS, all being significantly better that the commercial products tested by Shirtcliffe et al [6].

Figure 1. (a) Overlaid images of a snail moving up a vertical track bounded by the PDMS/soot material. **(b)** Two pots, one polypropylene and one PDMS/soot coated, both with snail food on top. **(c)** The same pots 24 hours after snails were admitted to the enclosure showing only the food on the polypropylene has been eaten.

Figure 2. The footprint area for young *helix aspersa* as a function of body mass.

One hypothesis by Shirtcliffe et al for the effectiveness of snails to adhere to and traverse a wide range of surfaces was that the mucus included a weak bio surfactant that was able to reduce the receding contact angle and create high contact angle hysteresis. The implication of this hypothesis is that a snail resistant superhydrophobic surface should be one that is able to maintain a high receding contact angle even when challenged by an appropriate surfactant. To characterise the wettability of the various surfaces, the receding contact angles various concentration of the anionic surfactant sodium dodecyl sulfate (SDS) were measured and the results are shown in figure 4. The most snail repellant material tested by Shirtcliffe et al (HIREC) is included in figure 4 and showed a high receding contact angle for low surfactant concentrations. However, as the surface tension of the SDS solution was reduced to below 68mN/m a transition occurred to a low receding contact angle. Soot/PDMS retains the high receding contact angle all the way down to an SDS solution surface tension of 48 mN/m before such a transition. This transition is consistent with the liquid entering the roughness of the superhydrophobic surface, which given the 10's nm length scales of the roughness for the soot surface can be expected to require higher concentrations of surfactant [8, 9].

3. Experimental Section

The soot/PDMS surfaces were produced in a similar method to previously described [8]. Rapeseed oil was left burning several minutes, using a wick, until a stable flame developed. Copper sheets were then placed at the top of a chimney, with a fan used to draw the soot up the chimney, until the entire surface of the copper was coated with a thick layer of matt black rapeseed oil soot. PDMS was mixed in a 10:1 ratio and degassed in a vacuum desiccator to remove any air bubbles trapped in the mixture. After approximately 30 minutes of degassing the PDMS was spread onto acrylic slides to the required thickness of 1mm. A prebake time of 30-35 minutes was used at 80°C until the PDMS became tacky. The soot coated slides were gently positioned, soot side down, onto the PDMS and a mass placed on top to ensure contact across the whole surface. These were then returned to an oven at 60°C for at least an hour. After cooling the acrylic slides and copper sheets were carefully removed from the PDMS surface leaving a PDMS membrane with a nanoparticle coating. Excess soot was then removed under running water in most samples although some were spin tested with the loose soot attached as shown in figure 3.

A zigzag track was produced on an acrylic sheet using sections of the soot/PDMS to mark the boarders. Young snails, helix aspersa (obtained from H & RH Escargots Kent UK) were placed at the bottom of the vertically mounted track and filmed with a video camera. A polypropylene container was covered by the soot/PDMS material and placed with an identical but uncoated container in an enclosure with fresh lettuce on top of each; these were also filmed over a period of 24 hours.

The snail centrifuge was a modified spin coated (Electronic Micro Systems Ltd. Salisbury UK) with a dc power supply used to power the motor and a tachometer used to measure the speed. A snail was placed 50mm from the center and the speed slowly increased until the snail was removed. This process was repeated for several snails on each of the different surfaces tested. Advancing and receding contact angles of sodium dodecyl sulfate (>99% Aldrich) in deionized water were measured using a Krüss DSA10 contact angle meter.

Figure 3. The removal force calculated from the spin speed at which the snails detached from a rotating horizontal disc, the snail mass and data from figure 2 for the footprint area for the different surfaces tested.

Figure 4. The receding contact angle of sodium dodecyl sulfate (SDS) solutions on PDMS/soot (black triangles), PDMS (red squares), polypropylene (blue triangles), Acrylic (purple diamonds), glass (green circles) and HIREC data from reference [6] (green triangles).

4. Conclusions

Soot/PDMS flexible membrane surfaces can be constructed and that they show excellent antiadhesive properties. Moreover, they also perform particularly well in resisting the ability of the anionic surfactant SDS to reduce the receding contact angle. This supports the hypothesis that an effective anti-adhesive snail resistant superhydrophobic surface is one that can maintain a high receding contact angle when challenged by an anionic surfactant, such as SDS.

Acknowledgments

NRG acknowledges Nottingham Trent University for provision of a PhD bursary.

Conflicts of Interest

The authors declare no conflict of interest.

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