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Surface treatment of polymer microfibrillar structures for improved surface wettability and adhesion

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ABSTRACT

The effects of altering the polymer surface characteristics on adhesion qualities of bio-inspired fibrillar adhesives were found to be significant. Treatment of fibril tip surfaces in polymer fibrillar adhesives improved their wettability and adhesion capacity. Surface modifications of fibril tips involved UV/Ozone and oxygen plasma treatments for making the fibril tips more hydrophilic. These surface treatment effects, however, tend to degrade over time (rendering hydrophobic recovery). The stability of treated (hydrophilic) surfaces was improved, while retaining their wettability, through coating with a polyelectrolyte such as polyethyleneimine (PEI) via self-assembly.

1. Introduction

Used by lizards and insects (including geckos, spiders, beetles, crickets and flies) to climb vertical and even inverted surfaces, the fine-hair (fibrillar) adhesive system is an excellent example of convergent evolution in biology. The density of surface hairs increases with the body weight of animal, and gecko has the highest hair density and the finest (nano-scale) hairs among all animal species that have been studied [1]. Gecko's nano-scale fibrillar structure develops high adhesion capacity with broad ranges of surface materials at high reliability levels [1–3].

The structure and unique capabilities of the gecko-foot have intrigued biologists and engineers for many years. Several investigations have been conducted into various aspects of the gecko-foot structure and behavior [4–6]. Current efforts to mimic gecko's adhesion mechanism can be divided into two broad categories: one uses arrays of relatively soft elastomeric fibrils such as polydimethylsiloxane (PDMS) and polyurethane (PU) [6,7]; the other uses arrays of high-modulus and high-aspect-ratio carbon nanotube or nanofibers [8]. While many investigators identify van der Waals interactions as the primary adhesion mechanism of fibrillar structures, some debate that capillary force, also contribute to gecko-foot adhesion to a variety of surfaces over a broad range of relative humidity [9,10]. Theoretical investigations indicate that capillary force can make important contributions to the adhesion capacity of fibrillar arrays [11,12], as this cohesive force is very large compared to van der Waals interaction [13]. In addition, adhesion against rough surfaces may benefit more from the capillary effect, as the capillary water bridging two surfaces is not significantly affected by the surface roughness [14]; the van der Waals force, on the other hand, is a distinctly short-distance force that is significantly affected by surface roughness. However, the highly hydrophobic nature of polymer microfibrillar structures is a disadvantage in building capillary bridges with the substrate [14].

Different surface modification techniques can be used to transform hydrophobic polymeric surfaces into hydrophilic ones. Examples of such techniques include multicomponent polyaddition reaction, corona discharges, oxygen plasma treatment, and UV irradiation with or without ozone [15,16]. UV/Ozone (UVO) treatment has been extensively applied to natural and synthetic polymers towards modification of the surface chemistry and wetting characteristics. It has been used for enhancement of interfacial adhesion in adhesive joints and composites [17]. UVO treatment is a photosensitized oxidation process which causes excitation and

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dissociation of polymer molecules by short-wavelength UV radiation; in addition, UV light dissociates oxygen to generate atomic oxygen which easily reacts with oxygen molecules to form ozone. The highly reactive ozone reacts with polymers to form polar functional groups, such as peroxyl, hydroxyl, carbonyl, etc., thus increasing the wettability of polymer surfaces [18]. Another approach to improvement of the water-wettability of polymer surfaces involves oxygen plasma treatment [16,19], which is environmentally friendly and easy to implement. Oxygen plasma treatment causes breakage of chemical bonds due to bombardment of the polymer surface with ions of high energy, and introduces polar groups to the polymer surface. UVO or plasma treatment of polymer surfaces can, under proper operating conditions, generate nanostructured surfaces [20]. This feature can be used to produce nano-fibrillar structures on micro-fibril tips, thus producing hierarchical structures which can, similar to gecko-foot, conform to surface roughness at different scales. However, hydrophobic recovery of oxidized polymer surfaces, caused by reversible relaxation processes of polar groups, can occur over time after UVO or oxygen plasma treatment of polymer surfaces. Other mechanisms can also contribute to this trend; in the case of PDMS, for example, migration of free siloxanes from the bulk to the surface through a porous or cracked hydrophilic silica-like layer contributes to hydrophobic recovery [21]. The hydrophobic recovery of polymer surfaces will affect its adhesion. Menezes and Doi studied adhering polymer molecules of desired qualities to treated polymer surfaces [15]. Stability of hydrophilic surfaces can be improved through coating with a polyelectrolyte with nano-thickness via self-assembly [22].

In this study, the polymer microfibrillar structures were treated with UVO and oxygen plasma to render stable changes in the fibril tip morphology and the hydrophilic qualities, and their effect on adhesion properties of polymer microfibrils were examined. The stable hydrophilic surfaces of polymer microfibrils were achieved through further coating of a thin layer of polyethyleneimine (PEI).

2. Materials and methods

2.1. Fabrication process of fibrillar arrays

2.1.1. Fabrication of silicon template

Fibrillar arrays were produced by soft-molding of elastomeric precursors on a micro-fabricated silicon template [23]; this versatile approach enables fabrication of fibrils with different dimensions. Photolithography was used to create the master template with pattern of holes with a diameter of 20 μm, a height of 20 μm and a center-to-center distance of 30 μm. For the purpose of fabricating the lithographic SU-8 templates, the silicon wafer was pretreated using a 3-step RCA cleaning process. The first step is performed by immersing the silicon wafer in a 1:1:5 solution of $NH_4OH + H_2O_2 + H_2O$ at 75 °C, and rinsing with DI water. Since the photoresist is hydrophobic, surface dehydration is performed to promote adhesion by baking in oven at 200 °C for 20 min. The SU-8 photoresist was then spin-coated on the silicon wafer at 2000 rpm. The thickness of the SU-8 film was verified using a DekTak^3 surface profiler. The patterns were created by the photo-lithographic process.

2.1.2. Soft-molding on the lithographic templates

Fibrillar arrays were made with polyurethane (PU) (ST-3040, BJB Enterprises, Inc) or polydimethylsiloxane (PDMS) (Sylgard 184, supplied by Dow Corning). The templates were silanized with heptadecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (hepta-fluorosilane). Gas-phase silanization was performed in an evacuated desiccator for 1 h, followed by baking at 95 °C for 1 h. Sylgard 184 prepolymer and cross-linker (at a ratio of 10:1) or PU ST-3040 A and B (20:17 by weight) was mixed, degassed, and then poured on the silanized template. The PU and PDMS were cured at room temperature and 65 °C, respectively, in light vacuum over 24 h, and then carefully demolded to avoid rupture of the polymer microfibrillar array. The total thickness of the elastomer sheet (with fibrillar surface) was approximately 1 mm.

2.2. Surface treatment of fibrillar arrays

A Photo Surface Processor (Model: PL16-110, SEN Lights Corporation) was used for UVO treatment of PU fibrillar arrays. The degree of UVO treatment can be controlled by the time of exposure and the distance to the sample. The fibrillar structures were treated for 30 min; this duration was selected through a trial-and-adjustment approach. Oxygen plasma treatment was carried out on PU and PDMS surfaces for 1–5 min at 1000 mTorr and an oxygen flow rate of 18.3 ml/min, using a Harrick Plasma Cleaner. To coat polymer fibrils with a thin layer of polyelectrolyte, a solution of 1 wt% polyethyleneimine (Aldrich) was prepared, with pH adjusted to 6.5, and the polymer fibrillar arrays, after oxygen plasma treatment, were placed in this solution over a 1-h period; it was then removed from the solution, rinsed with DI water, and dried under vacuum.

2.3. Surface characterization

Scanning electron microscopy (SEM, JEOL 6300F) and optical microscopy (DC5-163 digital compound microscope, National Optical) were used to study the morphology of polymer microfibrillar structures. Atomic force microscopy (AFM) surface imaging (Nanoscope IV Multimode SPM from Veeco) was also used to investigate the effect of surface treatment on fibril tips. Samples were scanned in tapping mode using an NSC 15 probe with nominal frequency of ~300 kHz and scan rate of about 0.5 Hz. Scans were performed at different scales in the range of 500 nm to 100 μm. Water contact angle measurement was performed using the sessile drop technique with a manual goniometer (Rame Hart, Inc Model 100-00 115 NRL-C.A.)

2.4. Adhesion test

Tension and shear adhesion capacities of 1 cm × 1 cm specimens of fibrillar arrays were measured against the substrates, including glass slides and polyvinyl chloride (PVC) films in a closed room with controlled humidity. A pulley setup built in house was used for the adhesion test. The substrates were sonicated in distilled water for 15 min, and then blow dried with N_2 gas. A preload pressure of 5 N/cm^2 was applied for 1 min to establish adhesion prior to performance of tension and shear adhesion tests. At least three samples were evaluated for each condition, and the standard deviation was calculated.

3. Results and discussion

3.1. UVO surface treatment

Fig. 1(a) shows a SEM image of PU fibrillar array with fibril diameter and length of 20 μm fabricated from the lithographic template. Fig. 2 compares the water contact angles of PU plain film and fibrillar array prior to and after UVO treatment. The water contact angle of the plain PU film is 73°, which is consistent with values reported in the literature (in the range of 65° to 75°) [18]. Therefore, the nature of PU surface is relatively hydrophobic. The PU fibrillar array shows a much higher water contact angle (120°), which can be attributed to the patterned surface morphology, similar to the lotus effect [24]. UVO treatment of PU plain film and fibrillar