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Poly(dimethylsiloxane) grafted with adhesive polymeric chains provide a route towards cost effective dry adhesives

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ABSTRACT

This study is aimed at developing an effective and potentially industrially applicable methodology for dry adhesion enhancement of bioinspired adhesive materials. Recently developed Activator Re-Generation through Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) was employed to graft poly(ethyl acrylate), poly(*n*-butyl acrylate) and poly(*n*-hexyl acrylate) polymer brushes on poly(dimethylsiloxane) (PDMS) substrates in presence of a structurally similar sacrificial initiator. Attenuated Total Reflection-Fourier Transformed Infrared spectroscopy (ATR-FTIR), Gel Permeation Chromatography (GPC), Nuclear Magnetic Resonance Spectroscopy (NMR), and ellipsometry were used to confirm the grafting and controlled growth of polymer chains on PDMS surfaces and in solution. A nanoindenter was used to measure adhesion on the PDMS samples at retraction rates of 10–50 nm/s and indentation depths of 100–500 nm. The polymer brushes were also grafted on PDMS micropillars of 20 μm in diameter with aspect ratio of 3, to test applicability of the developed method on bioinspired microstructured surfaces. A significant increase in adhesion was observed in all flat and micropatterned samples after the grafting resulting in achieving 20 kPa of adhesion strength in the flat samples. The study suggests that the investigated ARGET ATRP procedure can be used to produce cost effective dry adhesive surfaces.

1. Introduction

Strong and robust adhesion of gecko's feet has inspired numerous researches [1–3]. Utilizing the unique micro/nano sized features, arranged in hierarchical arrangement on its feet, geckos are able to make strong adhesive contact with almost any kind of surface [1,2,4,5]. Not only that the adhesion is strong, the attachment and subsequent release is easy and repeatable during the life of the lizards [3,6]. Such strong and robust adhesion is desirable for many industrial and biomedical applications [1,7,8].

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A large number of attempts to fabricate adhesives resembling the structure of gecko's feet have resulted in establishing various criteria to achieve strong and repeatable adhesion [9–11]. Among different parameters, having a very small diameter of the terminal feature of the synthetic adhesive pad is very important [12,13]. Different approaches have been adopted to achieve such small feature sizes, including use of photolithography [9,14], hot embossing [15], e-beam lithography [16], anodic aluminium oxide templates [17], porous nickel oxide templates [18] and reactive ion etching [19]. Some of these methods have been aimed towards large scale production of structured adhesives; however, due to high costs associated with these processes an industrial scale production has not yet been possible [20].

A highly dense fibrillar structure is required for enhanced contact area and increased adhesion [23]. A molecular scale approach to enhanced adhesive surfaces, that is otherwise possible only with nano-pillars, is by grafting of polymer chains from the biomimetic adhesives. Others and us have demonstrated improvement of adhesion by grafting flat and structured PDMS surfaces with poly(butyl acrylate) chains using Surface Initiated Atom Transfer Radical Polymerization (SI-ARTP) [21,22]. Grafting of high density poly(2-ethylhexyl acrylate) brushes by SI-ATRP for improvement of adhesion of photolithographically fabricated micro-pillars has been also demonstrated [24]. Grafting of polymeric chains onto structured adhesive surfaces may offer a cost effective route to high performance fibrillar adhesives. However, in the above mentioned studies, conventional ATRP methodology was utilized for grafting that has its limitation in regard to industrial scaling of the process, like requiring stringent reaction conditions and the use of large amounts of non-biocompatible catalysts [25]. Furthermore, so far the grafting has only been achieved from low aspect ratio microstructures, whereas grafting from high aspect ratio structures is highly desirable.

Oxygen tolerant version of ATRP, the Activator Re-Generation through Electron Transfer ATRP (ARGET ATRP) has been recently developed [26]. The key is the use of a reducing agent, which not only reduce oxygen radicals generated due to presence of oxygen, but also reduce Cu(II) catalyst to its active state (i.e. Cu(I)). Introduction of ARGET ATRP have made possible to synthesize polymers of controlled architecture on industrial scale, in presence of small amounts of oxygen and low amounts of catalyst [27].

The current study focuses on synthesis and characterization of microstructured biomimetic dry adhesives with high aspect ratio of the micro-sized pillars, using the approach of grafting of polymers from the surfaces by ARGET ATRP. Grafting process from a PDMS surface and the resulting adhesion properties were compared for grafting of poly(ethyl acrylate) (PEA), poly(*n*-butyl acrylate) (PBA) and poly(*n*-hexyl acrylate) (PHA) of a range of molecular weights. These polymers have low glass transition temperatures and low elastic modulus, considered as important for increased conformity and adhesion [28]. PEA, PBA and PHA were chosen to investigate the effect of the size of the alkyl side chain on the adhesion. Micropatterned PDMS surfaces with pillars of 20 μm diameters and aspect ratio ~3 were grafted with PEA brushes to demonstrate the applicability of this environmentally benign approach to prepare adhesive micro-patterned surfaces of larger surface area under less astringent conditions then used previously.

2. Experimental section

2.1. Materials

N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA), tin(II) 2-ethylhexanoate, copper(II) chloride ($CuCl_2$), 3-aminopropyltrimethoxysilane (APTMS) (**3**), triethylamine (TEA), chloroform, cyclopentanone, dicholoromethane (DCM), anisole, tetrahydrofuran (THF), ethanol, dimethylsulfoxide (DMSO), 2-bromoisobutyryl bromide (BIBB) (**5**), ethyl acrylate (EA) (**7**), *n*-butyl acrylate (BA) (**8**), *n*-hexyl acrylate (**9**), polystyrene Gel Permeation Chromatography (GPC) standards and propylene glycol monomethyl ether acetate (PGMEA) were purchased from Sigma-Aldrich. SU-8 2075 was purchased from Micro Chem. Sylgard-184 PDMS, which comes as two component kit (a base and a curing agent), was obtained from Dow Corning. Deionized water with resistance 18.2 MΩ was obtained from a Milli-Q water purification system. Prior to use, ethyl acrylate, *n*-butyl acrylate and *n*-hexyl acrylate were passed through a column of basic alumina to remove the inhibitor. All solvents in this work were used as received unless otherwise stated.

2.2. Procedures

2.2.1. PDMS functionalization

Components A and B of the Sylgard-184 kit were mixed in 10:1 and the mixture was poured in a mold to obtain desired thickness of the samples. The mixture was then cured at 60 °C for 24 h and the samples were then cut into test slides of 1×1 cm^2 (**1**). These test slides and silicon wafers were treated using oxygen plasma (see Section 2.3 for details and conditions) to obtain a surface covered with silanol groups (**2**). Oxygen plasma treated samples were immediately transferred to a solution of 0.2% APTMS in DMSO for 1 h, then sonicated for 5 min in chloroform to remove adsorbed substances, rinsed with water twice to obtain amino (—NH_2) functionalized samples (**4**). The samples were then heated in a vacuum oven at 120 °C for 1 h to promote crosslinking between PDMS and the silane and to remove any absorbed solvent residues. These amino functionalized substrates were then placed in a solution of BIBB (0.37 mL, 0.05 M, 3 mmol) and TEA (0.41 mL, 0.05 M, 3 mmol) in DCM (60 mL) at room temperature under N_2 and left for 1 h. The samples were then washed with DCM, sonicated in ethanol and dried at 60 °C under vacuum to obtain the initiator functionalized (—Br) samples (**6**) [29–31].