UNIVERSAL NANO-ADHESIVE OF PDMS OLIGOMERS

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ABSTRACT

A nanopatternable oligomeric PDMS layer has been first reported as a nano-interfacial adhesive for its intrinsic transferability and universal adhesiveness. Utilizing well-established PDMS surface modification and bonding techniques, we have been able to form an irreversible bond between a wide range of substrate pairs, representing ones within and across different material categories, including metals, ceramics, thermoset, and thermoplastic polymers.

INTRODUCTION

Joining heterogeneous surfaces has become a pressing issue in development of micro-nanoengineered systems, where multiple processing constraints have to be taken into consideration as a whole, e.g., specific material sensitivities to mechanical, thermal, and/or chemical treatments [1]. Based on the underlying physical and chemical mechanisms, existing bonding techniques can be divided into three major categories: thermal, chemical, and adhesive approaches. However, the material-dependent chemical bonding, and the structural deformation and passage blockage caused by thermal and adhesive bonding limit the applications of these existing bonding methods in micro-nanosystems [1]. Therefore, a simple bonding technique with general applicability to a wide range of material selections without structural distortion would be of particular attraction in building complex, multilayer micro-and nanostructures from different material types.

Recently, an intriguing mass transfer process has been reportedly discovered accompanying the microcontact printing process, that is, a nanometer-thick PDMS oligomer layer deposits on imprinted substrates with excellent adhesion [2]. The undesired oligomeric residues during the micro-contact printing process have shared several consistent characteristics, including 1) a nanometer-thick layer with intrinsic hydrophobicity (0.9-15 nm) [3], 2) excellent adhesion to the substrate (100 kPa to over 400 kPa), 3) ubiquitous presence upon contact with various substrates [2], and 4) strong dependence on interfacial physiochemistry (e.g., hydrophilicity and molecular polarity) [3].

In this paper, we utilize the intrinsic transferrable and adhesive natures of the PDMS oligomer layer as a universal, interfacial nano-adhesive to bond a group of commonly used micro-nanofabrication materials. Benefiting from the easy modification of PDMS surfaces, we have been able to form irreversible bonds (up to 400 kPa) between a wide range of substrate pairs successfully, representing ones within and across different materials categories, including metals, ceramics, thermoset and thermoplastic polymers. Moreover, the ultrathin adhesive layer of PDMS can be patterned with nanometer resolution by adapting the conventional microcontact printing strategy, which permits forming highly localized adhesion without compromising the existing structural dimensions. Universal nanoscale PDMS oligomer bonding can be achieved in two simple steps: surface hydrophilic modification and PDMS oligomer transfer to substrate pairs. Physiochemical properties of the PDMS oligomer layer and bonding strengths of various substrate pairs have been characterized experimentally with theoretical explanations proposed. Bonding tests show that interfacial adhesion strength approaching that of traditional PDMS-to-PDMS bonding can be realized across all material substrate pairs using the PDMS oligomer modification technique.

FABRICATION

The initial step began with hydrophilic modification of the substrate surfaces for PDMS oligomer transfer. Oxygen plasma treatment was performed to introduce hydroxyl groups on the targeted surfaces, followed by imprinting of oligomers from planar or micro-nanostructured PDMS stamps, during which the oligomer transfer happened only upon physical contact. Subsequently, both PDMS oligomer-coated substrates were treated by the second oxygen plasma (at 90 W for 30 s). Finally, two substrates were brought into contact by evaporating a DI water capillary bridge between them [4].

The thickness of micro-nanopatterned PDMS oligomer is measured by an iElli2000 imaging ellipsometer (Nanofilm, Germany) and atomic force microscopy (MFP-3D, Asylum Research). Contact angle measurement was conducted by placing a DI water droplet of 10 µl on the substrate and imaging with a digital stereomicroscope. Bonding strength of PDMS-assisted interfacial bonding was evaluated by standard blister test [5].

RESULTS

A theoretical model is proposed in Fig. 1 to explain the underlying mechanism of the universal bonding formation through the PDMS oligomer layers as an interfacial adhesive. The surfaces of the bonding pair are first treated with standard oxygen plasma for hydroxyl activation (Fig. 1a), followed by contacting with cured PDMS sheets (planar or patterned) for oligomer transfer (Fig. 1b). During the contact-printing step, a thin layer of unreacted divinyl PDMS oligomers, (i.e., uncrosslinked PDMS base, mer number = 20~90) [6], is transferred and immobilized onto the chemically functionalized substrates through potential chemical reactions between the vinyl and hydroxyl groups. Following removal of the PDMS stamps, both oligomer-coated surfaces are treated by the second oxygen plasma (Fig. 1c) and loaded face-to-face in intimate contact for covalent linkage formation (Fig. 1d).

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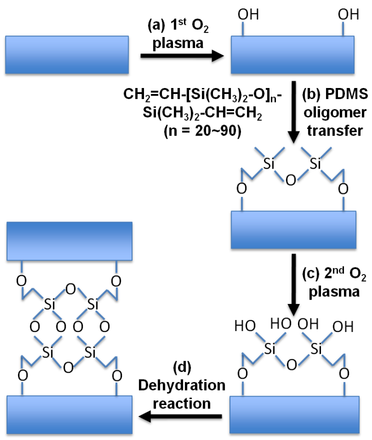

Figure 1: Theoretical model of the PDMS-assisted interfacial bonding. Surfaces are treated by oxygen plasma (a) for oligomer transfer (b) through PDMS/substrate contact. Oligomer-transferred surfaces are then treated by oxygen plasma (c) and bonded together (d).

According to the model, the interfacial adhesion formed through the nanometer-thick layers of PDMS oligomers is directly associated with the substrate-oligomer and oligomer-oligomer interfaces. To first investigate the properties of these two bonding interfaces, the effects of the processing parameters (i.e. power of oxygen plasma, contact duration, curing ratio and temperature of PDMS pre-polymers) have been characterized to control the interfacial physiochemical properties of the adhesive layers (e.g. surface chemistry and oligomeric thickness) and overall bonding strengths on a traditionally non-bonding PDMS/SU-8 pair.

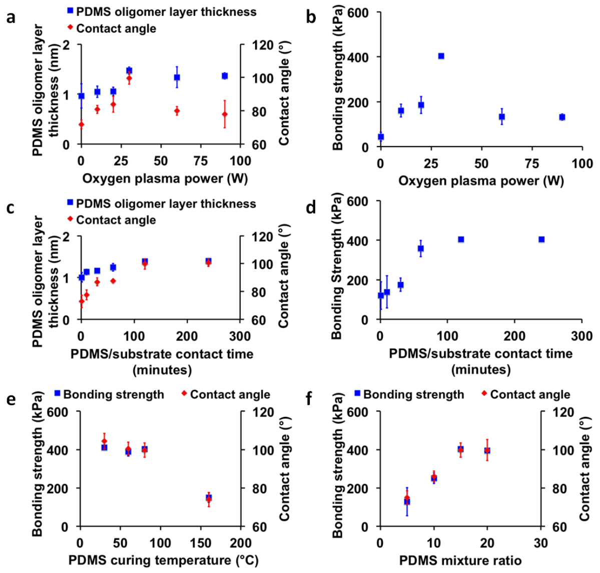

Figure 2: Experimental characterization and optimization of key processing parameters for the PDMS-assisted interfacial bonding.

As reported previously, PDMS oligomers are preferentially imprinted on hydrophilic surfaces rather than hydrophobic regions [7]. Oxygen plasma treatment provides a convenient way to render arbitrary substrates hydrophilic, which can promote the adhesion at the substrate-oligomer interface. Fig. 2a illustrates that surface hydrophilicity are influenced by the power level of oxygen plasma (in Fig. 1a). As can be seen, the contact angle of the SU-8 substrate and the thickness of the transferred PDMS oligomer layer vary with the plasma power (from 0 W to 90 W) at a given processing time (of 30 sec) with a similar trend, which links to the density of the activated hydroxyl groups, and the maximal values for both analyses are observed at 30 W experimentally. Continued oxygen plasma treatment at over 30W may over-oxidize the generated hydroxyl groups on the surface to a less reactive moiety [8]. More importantly, the differences in interfacial properties between materials may lead to a variation in bonding performance, as this process establishes the anchoring oligomer-substrate interface in the model. The observed bonding strength is closely correlated with the contact angle and oligomer thickness measurements and maximizes around 400 kPa at the same power level of 30 W, as shown in Fig. 2b. Accordingly, the contact angle and the oligomer thickness on the surfaces with no plasma activation are the lowest measured values, possibly indicating partial inhibition of the oligomer transfer by the hydrophobic nature of SU-8. In addition, the bonding strength on the control surfaces is substantially lower than that of the standard plasma-activated PDMS-to-PDMS bond, while substrates with complete oligomer transfer reach their full bonding strength potential, which reflects that plasma-generated hydroxyl groups dramatically promote the interaction between substrate surface and PDMS oligomer.

Fig. 2c and 2d summarize the interfacial impacts on the bonding quality by various contact duration between the PDMS stamp and the substrate (illustrated in Fig. 1b), during which oligomers diffuse from the bulk PDMS block to the interface. Fig. 2c shows the thickness measured by ellipsometry and contact angle with change of the contact time, both of which show positive correlations with increasing time. Based on our results, the contact angle changes more rapidly than that of the thickness, possibly due to the limited lateral resolution of ellipsometry, which only provides an average thickness over a microscale region and is insensitive to any nanoscopic features. However, the contact angle measurement can be highly sensitive to the interfacial properties of a surface both chemically and physically. Therefore, considerable rise in the contact angle with less than one hour contact time is likely due to increased coverage and uniformity of oligomers on the surface. After one hour, the substrate-oligomer interface becomes stable with little change in thickness or contact angle. Interestingly, the surface coverage takes place in a similar timescale to that of PDMS surface hydrophobic recovery after oxygen plasma treatment. The oligomer transfer process is consistent with our model, as the increased coverage of oligomers promotes the density of the chemical bond formation, yielding in an increase in the bonding strength, as demonstrated in Fig. 2d. As a result, the overall bonding strength rises from 100 kPa to 400 kPa prior to one hour and then reaches a maximum when the thickness and contact angle become stable with the extended contact time. These findings show that the contact time of oligomer transfer plays an important role in establishing a uniform adhesive layer, and significantly impacts the bonding performance at the oligomer-oligomer interface by increasing the bonding density between substrates. It is worth noting that according to the collective analyses in all processing parameters, the thickness of the oligomer layer has shown a consistently positive correlation with the bonding strength. It can be of particular importance to extend the range of intimate contact (typically within 1 nm) for intermolecular interaction (e.g. hydrogen bond) and further dehydration reactions between surfaces, given the presence of physical roughness on the surfaces.

In addition, processing parameters of PDMS stamps, such as mixing ratio of PDMS pre-polymer and curing temperature, are investigated and plotted in Fig. 2e and 2f to determine their role in the interfacial bonding. Decreasing the curing temperature and increasing the mixture ratio (of the base to curing agents) both lead to rising contact angle and improved bonding strength. Possible explanations of these trends are that more oligomers are present on the surface or an increase in oligomer diffusion rates permitted by the larger PDMS mesh size at lower curing temperatures and higher mixing ratios. These parameters will directly influence the quality of the substrate-oligomer interface by increasing the bond density, analogous to the effects of contact time in Fig. 2c.

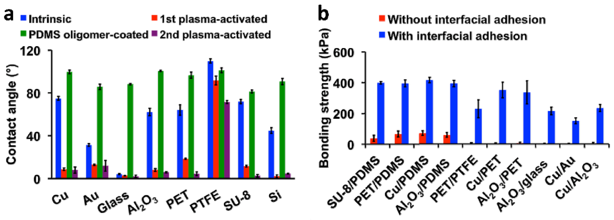

Figure 3: (a) Contact angle measurement to evaluate the interfacial property of various substrates prior to the bonding, and (b) experimental assessment on the interfacial bonding strength of various bonding pairs selected from (a).

Furthermore, universal applicability of the interfacial adhesion principle has been demonstrated on a number of traditionally hard-to-bond material pairs within and across the following material categories: metals (Cu and Au), semiconductors (Si), ceramics (Al_2O_3 and glass), and thermoplastic (PET and PTFE) and thermoset polymers (PDMS and SU-8), most of which are frequently used in micro-nanofabrication applications. As each material pair undergoes the bonding procedure shown in Fig. 1, contact angle measurements are made to infer the change of surface chemistry on the substrates, shown in Fig. 3a. All materials, except for the chemically inert PTFE, show a dramatic drop in contact angle after the 1^{st} oxygen plasma treatment, indicating that the surface energy has increased due to surface hydroxylation. Following the PDMS oligomer imprint step, the similarity of contact angle on different types of material surfaces, close to that of native PDMS, indicates that a layer of PDMS oligomer has been successfully transferred, providing a uniform surface chemistry for further activation and bonding. The subsequent oxygen plasma activation generates silanol groups on the PDMS oligomer layer and the following dehydration reactions upon contact will link the oligomer layers presented on both surfaces, analogous to the traditional PDMS plasma bonding technique.

As described in our model, the overall bonding strength between heterogeneous material pairs is limited by either the interfacial substrate-oligomer or oligomer-oligomer adhesion. The measured bonding strengths between a variety of different material types are summarized in Fig. 3b. It is clearly shown that the PDMS-assisted interfacial bonding technique can be not only extended to form strong adhesion between polymer and non-polymer substrates, but also among non-polymer pairs (e.g., Al_2O_3/glass, Cu/Au, and Cu/Al_2O_3). It can also be applied to conventionally hard-to-bond substrates (e.g., PTFE and PET). A relatively strong bonding of over 200 kPa has been repetitively shown using this approach. Among pairs that include one flexible polymer substrate (e.g. PDMS and PET), the bonding strength approaches a maximum of 400 kPa, approximating to the reported bonding strength of plasma-activated PDMS-to-PDMS bonding (180-715 kPa, 300 kPa in average), with the exception of PET/PTFE [6]. These indicate that the adhesion at the oligomer-oligomer interface determines the overall bonding strength among these bonding pairs. For the weaker bonding of the PET/PTFE pair, it is likely limited by the substrate-oligomer interaction, which is supported by the experimental observation of only slight changes in interfacial chemistry (implied by contact angle measurement) through the oxygen plasma treatment and oligomer imprint step, indicating that PDMS oligomer transfer was significantly inhibited by the intrinsic chemical inertness of PTFE. In addition, bonding strength between two stiff non-polymer substrates has been shown to be consistently lower than that of the pairs with a polymeric substrate. This phenomenon is likely explained by the rigidity of the materials and the presence of surface roughness, as any separation formed at the oligomer-oligomer interface will prevent the nanometer-thick oligomer layers from coming in close contact. However, the oligomer-substrate bonding strength is not likely to be the limiting factor in the non-polymer bonding pairs since significant changes in contact angle have been observed when the oligomer layer was transferred to those surfaces, similar to the change in contact angle of the polymeric substrate with excellent substrate-oligomer interface. Therefore, the overall bonding strength of mechanically rigid substrates is likely determined by the incomplete contact for interfacial bonding formation.

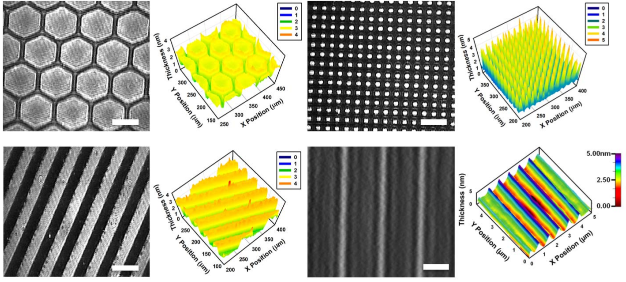

Figure 4: Transferred PDMS oligomer micropatterns (Ellipsometry, top and bottom left, scale bar: 50µm) and nanopatterns on single-crystal silicon substrates (AFM, bottom right, scale bar: 600nm).

Another impressive feature of the PDMS-assisted interfacial adhesion is that the oligomer layer can be microor nanopatterned onto substrates for highly localized bond formation through the microcontact printing process. Specifically, the desired patterns of oligomer transfer can be incorporated into a master mold of the PDMS stamp using a lithography-based technique. Subsequently, the molded PDMS is brought into contact with the bonding substrates. Only the embossed PDMS areas are in physical contact with the target substrates where the oligomer patterns are imprinted accordingly. Fig. 4 shows micro- and nanopatterns of PDMS oligomers formed on single-crystal silicon substrates, which can be captured by using an ellipsometry approach or an atomic force microscopy (note: the single-crystal silicon substrate is chosen as a reflective and atomically smooth surface for the analysis on the nanometer-thick imprinted oligomer layer). The imprinted oligomer layers present an edge effect, where the thickness along the border is always higher than that in the middle portion. This observation, consistent with previous reports on PDMS oligomer residues, could be potentially caused by the non-uniform diffusion of the PDMS oligomer from the patterned stamp that large amounts of PDMS oligomer dampen at the triple interface (substrate/air/PDMS) [9]. Furthermore, bonding performance of planar PDMS and SU-8 with a micropatterned oligomer layer (200 µm micropost array) has been experimentally evaluated (371.7±19.6 kPa), which delivers a comparable performance as that of the uniformly coated counterpart (398.7±8.5 kPa). The similarity of both bonding strengths demonstrates the robustness and patternability of the interfacial adhesive joining technique, which could be of particular use in creating micro-nanostructured surfaces and devices.

CONCLUSIONS

In this article, we have developed a universal PDMS-assisted nano-adhesive joining technique that utilizes the intrinsic transferrable and adhesive natures of the PDMS oligomer layer and facile surface modification to establish strong interfacial chemical linkage between heterogeneous substrate pairs. It offers distinct advantages over existing bonding techniques: (1) *Universal applicability* — high bonding strength (up to 400 kPa) can be achieved on various substrate pairs within or across different material categories using a standard process (oxygen plasma treatment and oligomer printing); (2) *Interfacial presence* — the imprinted PDMS oligomer layers are only within a few nanometers of thickness and have no direct impact on existing surface structures; (3) *Nano-patternability* — it is compatible with micro-nanopatterning techniques (e.g. micro-contact printing and stereomask lithography) and allows for highly localized adhesion formation; (4) *Process-compatibility* — it requires neither thermal nor mechanical treatment, which can be advantageous for biologically oriented applications. In summary, the simple universal bonding technique offers excellent bonding performance over a wide range of heterogeneous substrates and highly localized bonding formation with a nanometer precision, which can be readily employed in rapid-growing micro-nanoengineering applications.

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