Tribology International 114 (2017) 436–444

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Effect of capillary forces on the correlation between nanoscale adhesion and friction of polymer patterned surfaces

Prashant Pendyala[a], Hong Nam Kim[a], Harpreet S. Grewal[b], Il-Joo Cho[a], Eui-Sung Yoon[a,*]

[a] Center for BioMicrosystems, Korea Institute of Science and Technology (KIST), 02792 Seoul, Republic of Korea
[b] Department of Mechanical Engineering, School of Engineering, Shiv Nadar University, 201314, India

ARTICLE INFO

Keywords:
Adhesion
Nano-scale friction
Contact
Sliding

ABSTRACT

A general relation between adhesion and friction was elusive. This was partly due to the limitations in experimentally configuring the wide variety of geometrical and chemical cues encountered at a sliding contact. We study the combined influence of capillary and van der Waals forces on the correlation between the adhesion (pull-off force) and friction of polymer patterns. We report the existence of master curves in plot of adhesion *versus* friction, spanning nearly two orders of magnitude, characteristic of the effective lateral contact stiffness of the contact determined by geometry and capillary forces. Further, we showed how nanocylindrical patterns, micropatterns and PTFE-coated PMMA flat surfaces subjected to varying capillary forces displayed similar sliding characteristics despite their large differences in contact characteristics.

1. Introduction

Predicting friction under given physicochemical conditions is an interesting but complex engineering challenge. Comprehensive models that can predict friction under various physicochemical conditions are difficult to be established due to the complex interplay between the geometry and adhesion at the sliding contact [1,2]. In general, at macroscale, adhesion is assumed to be an external load in addition to the applied load. The total frictional force F between the interacting surfaces with an applied normal load L is [3–6].

$$F = \mu(L_o + L) = F_o + \mu L \quad (1)$$

where μ is the coefficient of friction and F_o is the friction force due to adhesion. Although, this interpretation holds for many of the experimental observations, it is not totally correct. Further, the dominant energy dissipating mechanism in macroscale sliding experiments may not be based on adhesion. But, at nanoscale, the influence of the van der Waals and surface forces makes the adhesion a dominant energy dissipation mechanism. Hence, relation such as the one shown in Eq. (1) may not hold at nanoscales.

Direct experimental correlation of adhesion and friction was difficult primarily due to the inability to measure the real area of contact due to the multi-scale roughness on the surfaces [7]. Hence experiments on surface interactions were being modelled in terms of single-asperity contact experiments [8] and simulations between flat atomic scale surfaces [9]. Surface force apparatus (SFA) and atomic force microscopy (AFM) where friction and adhesion could be simultaneously measured were used to study single asperity contacts under varied physiochemical conditions. Experiments with molecularly thin liquid films and self-assembled monolayers (SAMs) in SFA were used to study the relation between normal and lateral forces of a sliding contact [10,11]. Some experiments between rubber hemispheres and glass surfaces shear forces at the contact were found to be proportional to the adhesion hysteresis rather than adhesion [12,13]. Such relation was observed in the experiments with Langmuir-Blodgett films by Yoshizawa *et al.* [14] and in various other studies [15–17]. Further, many studies have used fracture mechanics analysis of single asperity contacts in correlating the normal adhesive forces to the tangential frictional forces [7]. However, a general relation between adhesion and friction is still elusive and requires intricate experiments understanding the interplay between geometry and chemistry at the contact.

The pull-off forces measured through AFM give a good estimate of the adhesion interactions at the stationary contact. van der Waals and capillary forces are the primary contributors to the total attractive force. However, despite the extensive studies on the effect of van der Waals forces on the sliding behavior [18,19], the dynamics of the capillary force in sliding requires further study [1,20,21]. Capillary forces due to the condensed water at the contact may significantly alter the behavior of the contact. The magnitude of capillary forces are observed to be comparable to that of van der Waals forces [22]. Effect of capillary forces on the contact between stationary contact is sufficiently understood by their modelling using idealized geometries

* Corresponding author.
E-mail address: esyoon@kist.re.kr (E.-S. Yoon).

http://dx.doi.org/10.1016/j.triboint.2017.04.045
Received 31 January 2017; Received in revised form 24 April 2017; Accepted 25 April 2017
Available online 02 May 2017

[23]. But understanding the role of capillary forces during sliding was difficult due to the complex geometrical interactions that vary the size, shape and distribution of meniscus at the contacting and non-contacting regions during the course of sliding [24]. This work explores how friction at the sliding contact subjected to varying capillary forces varies with respect to the measured adhesion.

Many studies have considered the role of the individual components of the contact, such as geometric and chemical factors, in the overall nanoscale contact interaction [25–30]. However, these studies cannot be directly compared or correlated to each other due to their large variety in samples and experimental conditions. This is in part due to the lack of fabrication techniques that can generate structures with varied geometric and chemical cues, especially at the nanoscale. We have recently used multi-step capillary force lithography [31] in tandem with nanodrawing [32] techniques to conduct a unique study investigating the effect of the curvature, height, surface energy, hierarchy, material, and pitch of the pillars on the adhesion and friction [33]. Because the fabrication procedures and geometric aspects were similar, the data obtained from the various patterns could be directly compared with each other. This work extends our previous studies to the humid experimental condition and investigates the role of capillary forces in determining the adhesive and sliding characteristics of multiscale patterned surfaces. To address this issue, the master curves were derived from the adhesion *versus* friction data. With these master curves, we demonstrate the role of local geometry and surface energy in modulating the relation between adhesion and friction under varying capillary forces.

2. Materials and methods

We fabricated three types of pillar-patterns: cylindrical, mushroom-shaped and hierarchical patterns. The parametric details of the pillar patterns along with the experimental details are listed in Table 1. The detailed fabrication procedure for the above patterns is given in Supplementary Material and can be found elsewhere [32,34,35]. Hierarchical patterns were generated using polymethyl methacrylate (PMMA). Cylindrical patterns with flat and round top morphologies were fabricated in both PMMA and polystyrene (PS). Flat- and round topped mushroom patterns were fabricated using PS alone. The surface energy of all the above patterns was varied using a thin surface coating (~20 nm) of polytetrafluoroethylene (PTFE).

The adhesion (pull-off force) and friction forces were measured using an atomic force microscope (AFM) (Multimode SPM, Nanoscope IIId, Digital Instruments). A borosilicate ball mounted on a cantilever of nominal spring constant of 0.58 N/m (Novascan Technologies, Inc.) was used for the measurements. The AFM ball tip roughness is in order of a few tenths of nanometer (can be seen as measured for Silica balls in Ref [36]), which was used in as obtained condition. For the friction measurements, normal load is varied from 40 to 120 nN at a sliding velocity of 5 μm/s. Relative humidity (RH) of the experiments were controlled from 5% to 80% using a custom built setup that utilizes anhydrous Calcium Sulphate ($CaSO_4$). Averaged values from 25 measurements were reported.

3. Results and discussion

The scanning electron micrograph (SEM) images in Fig. 1 show the geometry and arrangement (Table 1) of the patterns fabricated for the study. The fabricated patterns were superhydrophobic as demonstrated from the dynamic contact angle measurements shown in Fig. 2. Especially, the PTFE coated mushroom-shaped patterns exhibited minimal contact angle hysteresis. The detailed wetting characteristics of the patterns are discussed elsewhere [35,37]. We briefly present experimental results for the adhesion and friction in terms of the various physicochemical factors and then discuss the contribution of the capillary force in determining the sliding characteristics under changes in the other physicochemical factors. A detailed discussion on the effect of individual pattern parameters in the adhesion and friction behavior can be found in our previous works [33,37].

3.1. Adhesion and friction characteristics

In general, the adhesion force of the patterned surfaces was smaller by more than one order of magnitude compared to that of the flat surfaces (Fig. 3). Flat-top patterns showed higher adhesion than round-top patterns did due to the larger real contact area. Similarly, experiments with a larger ball tip radius showed higher adhesion (Fig. S1), and surface modification with a PTFE coating (20-nm thick) reduced the adhesion force by more than 10% for all the samples. Mushroom-shaped pillars showed a slightly smaller adhesion than did cylindrical pillars, which is inconsistent with the trends reported in the literature [26,38–41]. The hierarchical patterns, showed a 20 times lower adhesion than did the flat surfaces and an approximately 20–30% lower adhesion than did the nanopatterned surfaces.

Similar to the adhesion force measurements, the friction force measured for the patterned surfaces was significantly smaller than that of the flat surfaces (Fig. 4). The friction force values of PS flat and round-top pillar surfaces were 20–30% smaller compared to the corresponding values for PMMA surfaces. The mushroom-shaped pillars showed a 200% larger friction force than did the flat-top PS cylindrical surfaces, although the apparent contact areas of the two pillars were similar. Hierarchical patterns showed significantly reduced friction compared with that of both flat and nanopatterned surfaces and with an increasing pitch of the nanopillars, the friction further

Table 1
Geometric details of cylindrical, mushroom-shaped and hierarchical patterns along with the experimental conditions.

Pattern shape		Diameter (nm)		Height (nm)	Radius of curvature (nm)	Pitch (nm)	AFM tip diameter (μm)	Relative humidity (%)
Cylindrical (PMMA, PS)	Flat	250		220	–	500, 625, 750, 1000	10 (PS), 10 and 20 (PMMA)	40 ± 5
	Round	250		160	258	500, 625, 750, 1000		40 ± 5
Hierarchical (PMMA)	Micro	3000		2500	–	4000	20	5–80
	Nano	250		160	258	500, 625, 750, 1000	20	5–80
Mushroom-shaped (PS)	Flat	Flange Stem	250 100	550	–	500, 625, 750, 1000	10	40 ± 5
	Round	Flange Stem	250 100	550	512	500	10	40 ± 5