CHINESE PHYSICAL SOCIETY

Friction Properties of Bio-mimetic Nano-fibrillar Arrays *

CHEN Shao-Hua(陈少华)**, MI Chun-Hui(米春晖)

LNM, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190

Nano-fibrillar arrays are fabricated using polystyrene materials. The average diameter of each fiber is about 300 nm. Experiments show that such a fibrillar surface possesses a relatively hydrophobic feature with a water contact angle of 142°. Nanoscale friction properties are mainly focused on. It is found that the friction force of polystyrene nano-fibrillar surfaces is obviously enhanced in contrast to polystyrene smooth surfaces. The apparent coefficient of friction increases with the applied load, but is independent of the scanning speed. An interesting observation is that the friction force increases almost linearly with the real contact area, which abides by the fundamental Bowden–Tabor law of nano-scale friction.

Lots of reptiles possess an extraordinary ability to climb up vertical walls or roof ceilings. This kind of special ability attracts many scientists' research interests, in which geckos are mainly focused on due to their relatively large body weights. Experimental findings have shown that geckos' pads consist of arrays of sub-million setae and each seta splits into hundreds of nano-scale spatulae. The van der Waals and possibly capillary forces play a dominant role in such a fibrillar structure.[1−3] In order to understand geckos' adhesion mechanism and provide new methods for the design of novel adhesive materials, many adhesion and contact mechanics models have been developed, for example, Refs. [4–7]. Synthetic fibrillar adhesives have been attempted to be fabricated with several methods. The fabricated micro-fibrillar structures, such as stiff polypropylene micro-fiber arrays[8] and elastomer microfibers with spatulae tips,[9] have demonstrated that high static friction forces can be produced. As for the frictional properties of nano-fibrillar structures, Aksak *et al.*[10] proposed that vertically aligned multiwalled carbon nano-fibers could be a robust high friction fibrillar material, though they demonstrated that the interfacial molecular adhesion is too low to be considered in such a nano-fibrillar surface. In this Letter, we concentrate on combining the high friction property of polystyrene (PS) nano-fiber surfaces with the effect of interfacial molecular adhesion.

In the present work, polystyrene nano-fibrillar arrays are fabricated using membrane filters of Whatman Anodic aluminum oxide template with 300 nm nano-pores in diameter [Fig. 1(a)]. A layer of PS is spin-coated on a glass slide, then covered by the porous membrane and heated at 80°C in a vacuum oven for three hours. Finally, the membrane is etched away using NaOH solution in 24 h. A typical scanning electron microscope image of the fabricated nano-fibrillar arrays is shown in Fig. 1(b), in which a single PS fiber is about 300 nm in diameter, 3 μm in average length and the volume fraction of fibers is about 65%. Lateral adhesion that should be avoided in our subsequent fabrications is found in the present samples. As pointed out in Refs. [7,11], for a given fibrillar arrays, there exists a critical length of L_{cr}, beyond which the surface adhesive forces may cause neighboring fibers to bundle together. The critical length for the PS nano-fibrillar arrays is calculated to be $L_{cr} = 1.967$ μm. Compared to the average length of fibers 3 μm in the present sample, it is required for us to reduce the fiber length in future designs.
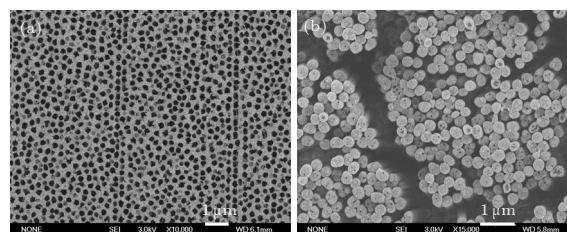

Fig. 1. (a) Whatman Anodic membrane filters and (b) SEM image of fabricated PS fibrillar arrays. The diameter of a single fiber is about 300 nm and the length is about 3 μm. The volume fraction of fibers is about 65%.

The wettability of the fabricated nano-fibrillar arrays is characterized using Dataphysics OCA20. The measured contact angles of the present PS nano-fibrillar surfaces and the corresponding PS smooth surface with water are shown in Figs. 2(a) and 2(b), respectively. It is clearly seen that the contact angle of the fibrillar arrays is about 142°, while that of the PS smooth surface is only about 89°. This kind of effect should be attributed to the surface

**To whom correspondence should be addressed. Email: chenshaohua72@hotmail.com

micro-structure and micro-morphology, analogous to the super-hydrophobic phenomenon that occurs on lotus leaves.
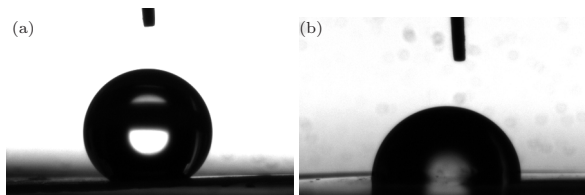

Fig. 2. (a) A droplet of water on a fabricated PS nano-fibrillar array and (b) on a smooth PS surface.
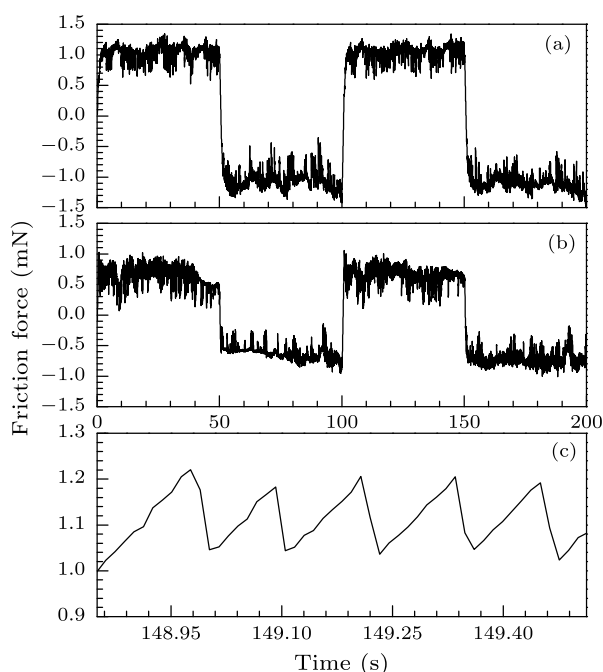

Fig. 3. (a) The friction force on a fabricated PS nano-fibrillar array as a function of the time measured by reciprocating motions and (b) the friction force on a smooth PS surface as a function of the time. The normal preload is $1200\,\mu$N and the scanning speed is $10\,\mu$m/s. (c) The local amplified plot shows a zigzag phenomenon due to adhesion.

Micro-scale frictional performance of the fabricated nano-fiber arrays is characterized by using a ball-on-flat type micro-friction instrument (State Key Laboratory of Tribology, THU) under reciprocating motions. A smooth siliconnitride sphere with 4 mm in diameter is attached to a load cell and moved vertically until reaching a pre-specified normal load. Then the sphere moves horizontally, during which the sphere maintains its fixed position. The disturbance of the environmental noise is effectively avoided. Friction force is measured under a set of applied normal loads and sliding speeds.

The results show that the friction force fluctuates periodically during reciprocating motions and the amplitudes in different cycles do not show a significant difference. Typical curves of the friction force vs the

loading time for a fabricated nano-fibrillar surface and a flat surface are shown in Figs. 3(a) and 3(b) under a normal preload of $1200\,\mu$N and a scanning speed of $10\,\mu$m/s. Comparing Figs. 3(a) and 3(b), one can see that the measured apparent coefficient of friction of the PS nano-fibrillar surface is much larger than that of the flat surface. If we define the friction force in two forms as $f = \bar{\mu}P$ and $f = \mu(P + P_{ad})$, where $\bar{\mu}$ and μ are apparent and real coefficients of friction, respectively, P and P_{ad} are the normal preload and the adhesion force, a larger apparent coefficient of friction will be yielded due to the adhesion force. Actually, local amplification of the curve in Fig. 3(a) clearly shows a typical zigzag [Fig. 3(c)] and demonstrates significant adhesion between the siliconnitride sphere and the sample, which has also been found by Wang et al.[12] in the measurement of interactions between AFM tips with various radii and nano-particles.
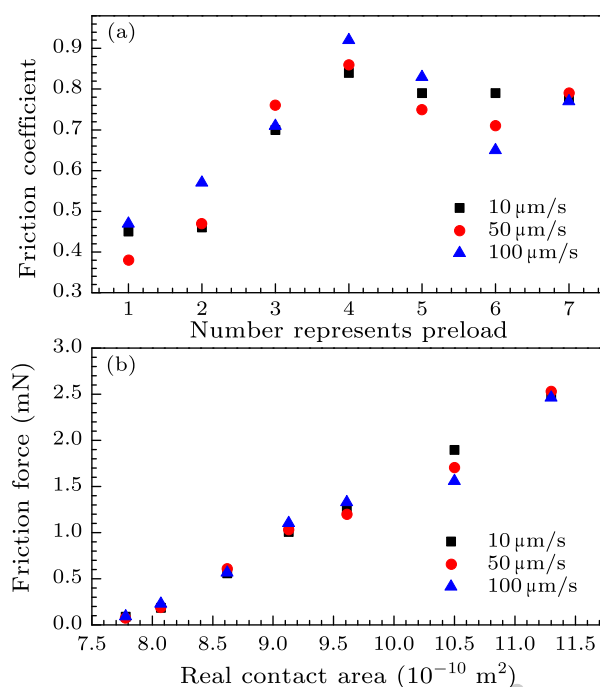

Fig. 4. (a) Relation between the coefficient of friction of PS nano-fibrillar surface and the normal preload for different scanning speeds. Numbers from 1 to 7 on the x axis represent the normal applied loads $200\,\mu$N, $400\,\mu$N, $800\,\mu$N, $1200\,\mu$N, $1600\,\mu$N, $2400\,\mu$N, $3200\,\mu$N, respectively. (b) Friction force under different preloads as a function of the real contact area.

Figure 4(a) shows the measured coefficient of friction as a function of the normal preload and sliding speed. From Fig. 4(a), one can see that the coefficient of the fabricated nano-fibrillar arrays does not depend on the sliding speed. However, the coefficient of friction increases with the applied normal load and a maximum value exists at a critical load, after which the coefficient of friction shows a slowly downward trend. Why does the normal preload influence the coefficient of friction of nano-fibrillar surfaces? The main fac-

tor is the number of nano-fibers in adhesive contact with the siliconnitride sphere. Before the instability of nano-fibers, the contact area increases with the applied normal preload and the contact area directly affects the adhesion force, thereby increasing the apparent coefficient of friction.

The adhesion energy per unit contact area is measured to be $\Delta\gamma = 0.1698\,\mathrm{J/m^2}$ using AFM and the classical JKR model.[13] In order to obtain the real contact area, $0.1698\,\mathrm{J/m^2}$ is approximately regarded as the adhesion energy per unit contact area between the siliconnitride sphere and the fibrillar sample. As a typical composite, the fabricated nano-fibrillar array is assumed to be an approximately isotropic solid with an effective Young's modulus of $0.65E_{PS}$, where E_{PS} is Young's modulus of PS. The contact radius under the normal preload complies with the classical JKR solution, $a_{\mathrm{JKR}} = \left\{\frac{3R}{4E^*}[P + 3\pi R\Delta\gamma + \sqrt{6\pi R\Delta\gamma P + (3\pi R\Delta\gamma)^2}]\right\}^{1/3}$, where R is the radius of the siliconnitride sphere, P is the normal preload and E^* is an effective modulus.[13] A rough estimation of the real contact area is found to be $0.65\pi a_{\mathrm{JKR}}^2$. Thus, the friction force can be obtained as a function of the real contact area as shown in Fig. 4(b), in which it is very interesting to find that the friction force increases almost linearly with the real contact area. It is suggested that the friction force is directly dependent on the real contact area for the fabricated nano-fibrillar arrays and abides the fundamental Bowden–Tabor law of nano-scale friction, i.e. $f = \tau A_r$, in which τ is the sheer strength of the contact interface and A_r the real contact area.[14]

In conclusion, PS nano-fibrillar arrays have been fabricated with about 300 nm in diameter of each fiber, and we have shown a hydrophobic feature with contact angle $142°$. In contrast to a smooth PS surface, the enhanced friction force and apparent coefficient of friction are significantly influenced by the normal preload and interfacial adhesion, but insensitive to the scanning speed. Approximate analysis suggests that the fundamental Bowden–Tabor law of nano-scale friction could predict the experimental friction results. Future work includes the reduction of the nano-fiber's length according to the anti-bunching condition, variation of the diameter of the scanning sphere with a similar idea to Wang et al.,[12] and peeling tests to study the normal adhesion properties of nano-fibrillar surfaces.

References

[1] Autumn K, Liang Y A, Hsieh S T, Zesch W, Chan W P, Kenny T W, Fearing R and Full R J 2000 Nature 405 681
[2] Huber G, Gorb S N, Spolenak R and Arzt E 2005 Biol. Lett. 1 2
[3] Autumn K, Sitti M, Liang Y A, Peattie A M, Hansen W R, Sponberg S, Kenny T W, Fearing R, Israelachvili J N and Full R J 2002 Proc. Natl. Acad. Sci. U.S.A. 99 12252
[4] Arzt E., Gorb S and Spolenak R 2003 Proc. Natl. Acad. Sci. U.S.A. 100 10603
[5] Chen S H and Gao H J 2007 J. Mech. Phys. Solids 55 1001
[6] Chen S H and Soh A K 2008 J. R. Soc. Interface 5 373
[7] Glassmaker N J, Jagota A, Hui CY and Kim J 2004 J. R. Soc. Interface 1 23
[8] Majidi C, Groff R E, Maeno Y, Schubert B, Baek S, Bush B, Maboudian R, Gravish N, Wilinson M, Autumn K and Fearing R S 2006 Phys. Rev. Lett. 97 076103
[9] Kim S, Aksak B and Sitti M 2007 Appl. Phys. Lett. 91 221913
[10] Aksak B, Sitti M, Cassell A, Li J, Meyyappan M and Callen P 2007 Appl. Phys. Lett. 91 061906
[11] Yao H and Gao H 2006 J. Mech. Phys. Solids 54 1120
[12] Wang P, Yang H J, Wang H B, Li H, Wang X Y, Wang Y, Lu J H, Li B, Zhang Y and Hu J 2008 Chin. Phys. Lett. 25 2407
[13] Johnson K L, Kendall K and Roberts A D 1971 Proc. R. Soc. London A 324 301
[14] Yoon E S, Singh R A, Oh H J and Kong H 2005 Wear 259 1424