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Large-Scale Equal-Proportional Amplification Bio-Replication of Shark Skin Based on Solvent-Swelling PDMS

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ABSTRACT: Shark skin has attracted worldwide attention on its superior drag reduction, so-called shark skin effect. Such marvelous function of shark skin, in particular, is in part related to complicated micro-riblets. As the creation of natural evolution, micro-riblets of shark skin act out desirable drag reduction only within range of swimming speed. Over past few years, bio-replication approach which takes the shark skin as replica template to 1 : 1 transfer surface morphology has been widely applied for drag reduction. However, if application environment remarkably differs from living environment, the drag reduction function is attenuated or even becomes adverse, i.e., the surface structure nonadjustable to ambient environment is obstacle to widespread application of bio-replication. In this paper, large-scale equal-proportional amplification bio-replication approach is presented to adjust the micro-riblets of shark skin by taking solvent-swelling polymer as replica mould. Solvent-swelling property of polymer is investigated by controlling its swelling ratio to make natural surface function adapting to various application environment. Apart from higher replication accuracy about 95%, experiments show that about 140% solvent-swelling ratio is achieved at one-time amplification, and translation of drag reduction peak of natural surface function form living environment to various application environments is ensured by successive large-scale equal-proportional bio-replications. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 2383–2389, 2013

KEYWORDS: biomimetic; swelling; molding; manufacturing

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INTRODUCTION

With the spread of energy crisis and pollution, drag reduction technology has attracted worldwide attention as an effective strategy to save energy.[1,2] Living creatures in nature have non-smooth surfaces, which usually have superior functions such as anti-adhesion, hydrophobicity.[3,4] At 1960s, shark was observed that its skin has remarkable superior drag reduction effect, so-called "shark skin effect." That was because micro riblets were formed over whole body by perfect alignment of tiny placoid scales.[5] Under such inspiration, Walsh[6] investigated several different types of riblet surfaces and experimentally found that the drag reduction of a symmetric V-groove riblet was about 8%. Choi et al.[7] compared near-wall structure over smooth and grooved surface, and clarified that the restriction of spanwise movement of the longitudinal vortices was prime mechanism of drag reduction over riblet surfaces. Bechert et al.[8] built adjustable surface with longitudinal blade ribs and with slits on basis of systematic experimental optimization, providing a maximum benefit of a 9.9% decrease in fluid drag. Boeing and Airbus[9] eventually led to trials on aircraft coated with a plastic film with riblets, and demonstrated about 8% drag reduction. Büttner et al.[10] investigated possible fabrication methods for riblets in the micrometer regime for high temperature applications, and realized wall shear stress reduction of up to 4.9%. Almost all of these biomimetic drag reduction studies took idea from shark skin, in which longitudinal V/U-groove riblet was set parallel to flow direction and the maximum drag reduction was confined to specific fluid velocity region.

Extreme simplification was normally conducted to build biomimetic riblets due to lack of feasible fabrication approach to complex natural surface morphology such as shark skin. It is undoubtedly that structural simplification usually results in drag reduction function decline. To resolve such problem, bio-replication, which directly take natural surface as replica

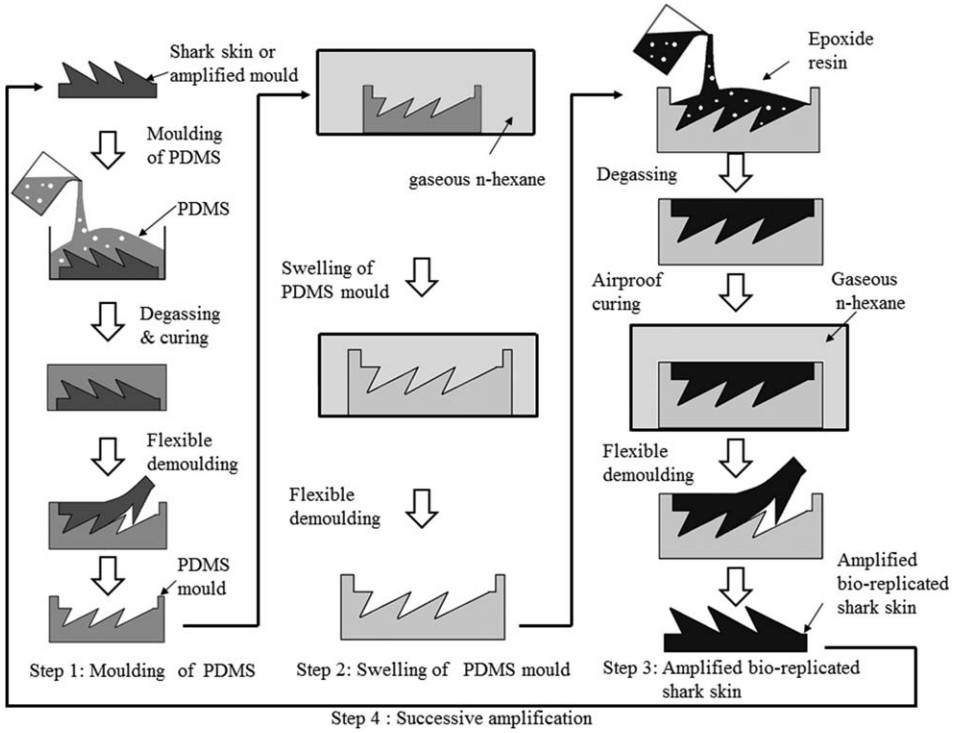

Figure 1. The process of *LsEp* amplification bio-replicated shark skin by solvent-swelling PDMS in gaseous *n*-hexane.

template to 1 : 1 transfer its surface morphology, has been proposed to take as full advantage of natural surface function as possible. Zhang et al.[11–13] took natural shark skin as replica template to duplicate superior drag reduction surface, and experimentally proved that not only the duplication accuracy reached to 95%, but the maximum drag reduction was improved up to 12%, larger than U/V-groove riblet. Oeffner et al.[14] also illuminated that shark skin membranes show a mean 12.3% increase in swimming speed compared with the same skin foils after removing the denticles.

Adaptation to living environments is the driving force of natural evolution, accordingly drag reduction of shark skin works to the max just at its living environment. Bio-replicated shark skin performs maximum drag reduction about 12% only when relative fluid flow is around 5 m/s,[1] which indicates optimal drag reduction fluid velocity of shark skin around 5 m/s. Therefore, adjusting optimal drag reduction fluid velocity region via controllable surface modification is very necessary to spread industrial application. According to Walsh's observation that maximum drag reduction of micro-riblets is dependent on optimum spacing s^+ and is affected by depth-to-width ratio *h/s*, equal-proportional scaling of surface morphology is one way to guarantee maximum drag reduction of bio-replicated shark skin remaining at different application environments.

Bio-replication forming approach is based on replica mould process, thus large-scale equal-proportional amplification (*LsEp* amplification hereafter) can be fabricated if female mould materials have swelling property. Superior microscopic surface structure and large-scale swelling are two important demands for swelling material to ensure translation of excellent natural surface function.[15] Nevertheless, few materials meet the demands so far, for example, some metals and ceramics[16,17] can be amplified to some degree due to thermal expansion effect, but the expansion coefficient is too low. Other materials such as copolymer hydrogels[18] and sponges[19–21] can be large-scale swollen in water, but micro-pores swell simultaneously to destroy original microscopic surface structure. Fortunately, polymer science has made great progress by worldwide R&D, especially in development of novel polymer materials over past decades. Among their specific properties, large-scale swelling is one long-term pursuit. For example, polydimethylsiloxane (PDMS), as one type of cross-linked polymers, generally swell to large scale in response to some organic solvent like *n*-hexane.[22–25]

In an effort to solve the drag reduction riblet nonadjustable problem of bio-replicated surface, one novel *LsEp* amplification bio-replication is proposed by taking advantage of PDMS swelling effect, especially for accurate swelling control of shark skin micro riblets. In this article, the *LsEp* amplification bio-replication process is illustrated briefly, and the solvent-swelling effect of PDMS in gaseous *n*-hexane is quantitatively investigated. *LsEp* amplification of shark skin is conducted by twice successive bio-replication. Especially, the possibility of accurate controllable amplification bio-replication via solvent-swelling PDMS is revealed by bio-replication experiments. Finally, the translation of maximum drag reduction for various application environments is proved by test in water tunnel.

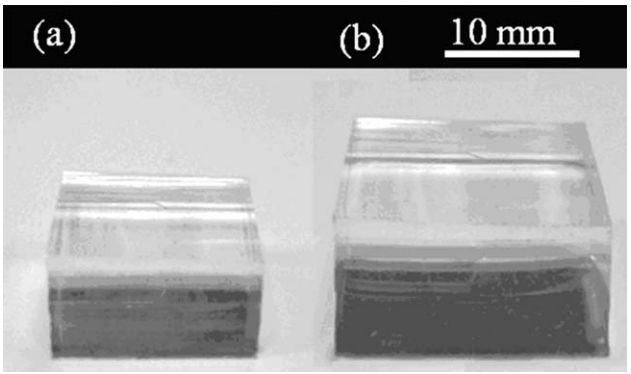

Figure 2. The swelling PDMS mould, (a) the original PDMS mould, (b) swollen PDMS mould in gaseous *n*-hexane.

LSEP AMPLIFICATION BIO-REPLICATION PROCESS OF DRAG REDUCTION SHARK SKIN

Bio-replication process generally comprises of three sub-steps, i.e., preparation of shark skin template, PDMS female mould, and biomimetic shark skin fabrication. The size and accuracy of bio-replicated drag reduction riblets is greatly dependent on manipulation of female mould. The *LsEp* amplification bio-replication becomes possible if the solvent-swelling polymer such as PDMS is used as material of female mould. Consequently, the *LsEp* amplification bio-replication of drag reduction riblets can be proposed as shown in Figure 1, among which the swelling of PDMS female mold in gaseous *n*-hexane is inserted into traditional bio-replication as second step. Accurate control of solvent-swelling of PDMS female mould is inevitable to achieve high-precision bio-replicated drag reduction riblets. Larger proportional amplification of drag reduction riblets can be achieved by repetitious successive amplification replication.

The PDMS female mould is placed in an airtight container filled with certain concentration of gaseous *n*-hexane for a certain time. The swelling ratio and rate of PDMS female mould is determined by concentration of the gaseous *n*-hexane. The swollen PDMS female mould is taken out as replica template, upon which epoxide resin is poured and degassed for 3 min. The poured female mould is remained again in the airtight container filled with gaseous *n*-hexane until epoxide resin full cured.

Polydimethylsiloxane (PDMS) elastomer kits (Sylgard 184) were purchased from Dow Corning (Midland, MI). Simethicone and *n*-hexane were used as mold releasing agent and swelling solvent, respectively, in this experiment. Epoxide resin (Model: XY-2) was taken as material of thin film to produce biomimetic drag reduction surfaces, and a vacuum chamber (DZF-6020, Shanghai) was prepared to squeeze the air out of cavities of shark skin. Deionized water was used as received. The whole experiment is taken at 28°C, and the saturated vapor pressure of *n*-hexane at 28°C is 24 kPa, which means the highest *n*-hexane concentration is approximate 0.85×10^{-3} g/mL.[26]

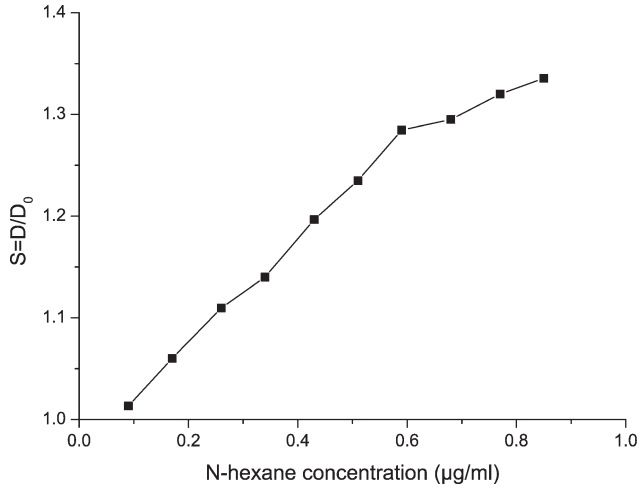

Figure 4. The best swelling ratios at different gaseous *n*-hexane concentration.

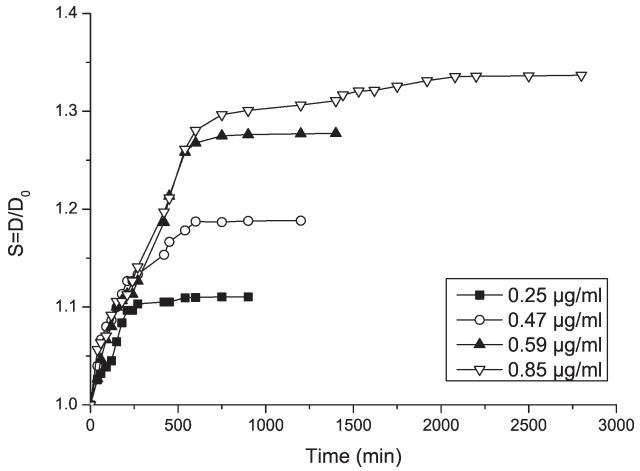

Figure 3. The swelling behavior of PDMS in gaseous *n*-hexane (D_0 is the original size of the PDMS mould, D is the amplified size of the PDMS mould, $S = D/D_0$).

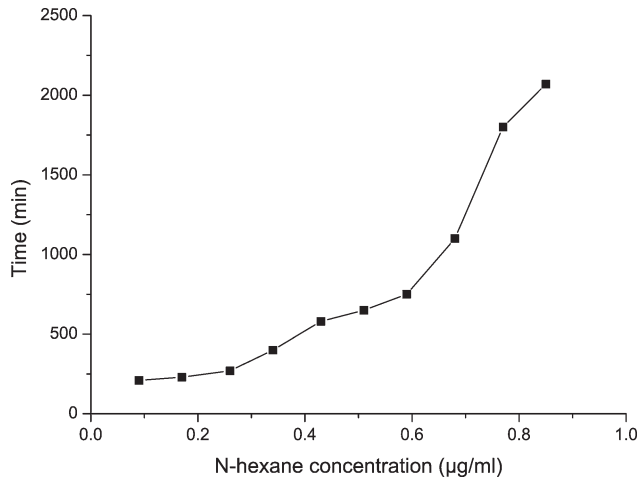

Figure 5. The time PDMS spends to reach the best swelling ratio at different gaseous *n*-hexane concentration.

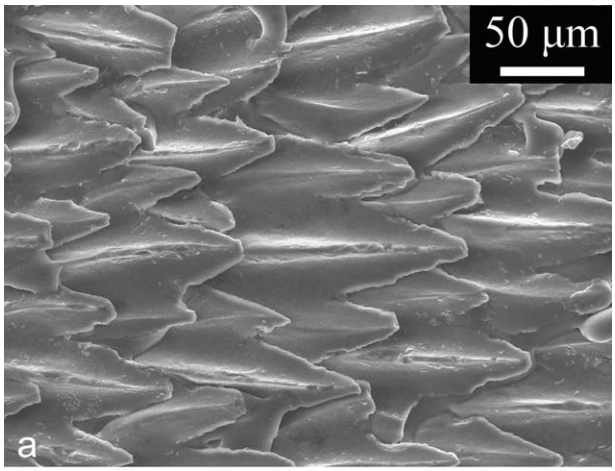

Figure 6. SEM images of the shark skins, (a) the real shark skin, (b) negative mould for bio-replication.

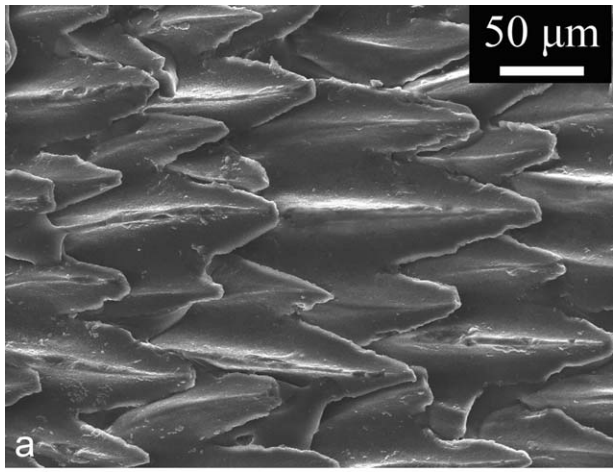

Figure 7. SEM images of the shark skins, (a) first-time amplified shark skin, and (b) second-time amplified shark skin.

RESULTS AND DISCUSSION

Swelling Control of PDMS Female Mould

The thickness of PDMS mould is set 5 mm, whose length or width has been experimentally proven no obvious affect on swelling ratio and swelling rate. In experiments, the size of the PDMS mould sample is 15 mm × 15 mm × 5 mm.

The PDMS mould swells to large scale in gaseous *n*-hexane, and the optimum swelling ratio of PDMS reaches about 34% in gaseous *n*-hexane as shown in Figure 2. In the gaseous *n*-hexane, the concentration of *n*-hexane plays great role in swelling ratio and swelling rate. The volume of PDMS sample gradually swells along with maintaining time in gaseous *n*-hexane as shown in Figure 3. Although the swelling rate differs depending on *n*-hexane concentration, the behavior of PDMS mould swelling in size is similar, i.e., PDMS mould swells rapidly at initial stage and finally remains stable. Because the swollen PDMS is taken as female mould in step 3, swelling to volume stable state is inevitable for accurate formation of function surface. The PDMS sample takes at least 10 h to reach the highest point of swelling behavior and keeps stable in volume afterwards, which point is called best swelling ratio hereafter. Figure 4 shows the best swelling ratio at different gaseous *n*-hexane concentration. It can be seen that the best swelling ratio of PDMS improves with increase of gaseous *n*-hexane concentration. The maximum concentration of gaseous *n*-hexane stops at 0.85×10^{-3} g/mL as saturated vapor pressure at 28°C. The swelling behavior stops around 34% at state of saturated vapor pressure, which is the maximum swelling ratio in all concentrations of gaseous *n*-hexane at 28°C. Thus, the swelling ratio of amplification bio-replication can be controlled by elaborative choice of *n*-hexane gaseous concentration.

Solvent-swelling of PDMS generally is a slow process, taking longer time to reach best swelling ratio. The spending time of PDMS swollen to best swelling ratio in general increases with volume swelling ratio. The PDMS mould swelling to best swelling ratio (34%) at 0.85×10^{-3} g/mL maximum concentration of gaseous *n*-hexane spends longest time, about 2000 min as shown in Figure 5. Swelling to stable state of volume is necessary to achieve high-precision bio-replication, thus the swelling time of PDMS mould can be determined from Figure 5.

Replication Accuracy of *LsEp* Amplification Bio-Replication of Drag Reduction Shark Skin

The biomimetic shark skin is fabricated in the step 3 of bio-replication by pouring epoxide resin upon swollen PDMS mould. Figure 6 shows the real shark skin and its PDMS negative mould. Figure7 shows the bio-replicated biomimetic shark skins

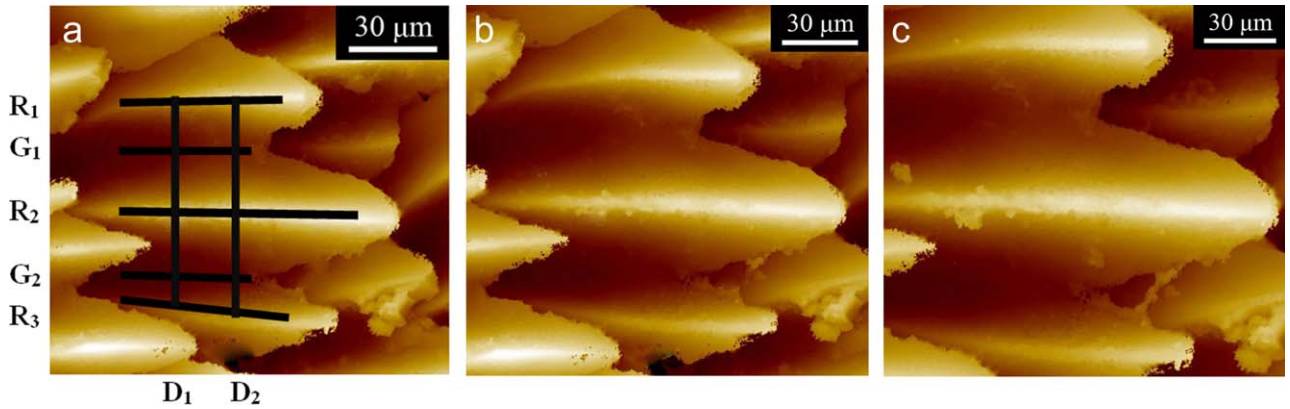

Figure 8. The 3D white light interference images of (a) the real shark skin scale, (b) its corresponding first-time amplification bio-replicated shark skin, and (c) its corresponding second-time amplification bio-replicated shark skin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of first-time amplification and second-time amplification at 0.85×10^{-3} g/mL gaseous *n*-hexane, respectively. By comparison between original and amplified shark skins, we can see that the template is amplified in equal proportion and the micro morphologies of amplified bio-replicated shark skin surfaces are remained satisfactory. Because the amplification ratio of each time bio-replication is about 34%, the second-time bio-replication can make surface morphology amplified up to about 80%.

To quantitatively analyze *LsEp* amplification bio-replication accuracy, surface morphology was scanned by means of 3D white light interference profilometer (Model: SOHIO, AEP Technology, USA) as shown in Figure 8.[27]. All the samples were sputtered with a layer of Au (*ca.* 2 nm thick) to improve reflecting performance. The main structure of a shark skin scale is made up of three ridges and two grooves, whose characteristic parameters are obtained to assess amplification bio-replication accuracy. The locations of surface curves are labeled by black lines as shown in Figure 8, where $R_{i(i\ =\ 1,2,3)}$ and $G_{i(i\ =\ 1,2)}$ separately represent scale ridges and grooves, and $D_{\ i(i\ =\ 1,2)}$ the vertical curve over the scale. The amplified bio-replications are contracted by its amplification ratio 1.34 for first-time amplification and 1.80 for second-time amplification in every direction to make them uniform in scale. If *LsEp* amplification bio-replication accuracy is higher, surface morphology of real shark skin will be closer to contracted bio-replicated shark skin. The characteristic curves of real shark skin and its corresponding contracted bio-scaled shark skins are separately shown in Figure 9. The value difference represents the bio-replication error which can be statistically accumulated from 90 points over lines. Error statistic shows that the average error is 0.0173 μm and the maximum error is 0.49873 μm for first-time amplification bio-replication, and average error is 0.01809 μm and the maximum error 0.50461 μm for second-time amplification bio-replication, which indicates bio-replication accuracies are higher than 95% although accuracy decreases with increase of bio-replication times.

Drag Reduction of LsEp Amplification Bio-replicated Drag Reduction Shark Skin

In order to validate translation of optimal drag reduction fluid velocity region of shark skin via *LsEp* amplification bio-replication, the experiment was conducted in vacuole water tunnel of China Ship Scientific Research Center (CSSRC). The length of the test section in vacuole water tunnel is 3.2 m with diameter 0.8 m. The measurement range of strain gauge balances is 300 N and its resolution is 0.1 N. Test model with hollow elliptical sphere at front end and hollow cylinder at posterior segments is made from aluminum alloy LY12, whose size is 90 mm in external diameter and 500 mm in cylinder length. The size of mold used to produce test skins is 83 mm $\times$ 200 mm $\times$ 5 mm. The test skins are made from waterborne epoxy resin, which including smooth skin, real shark skin, first-time amplification bio-replicated skin, and second-time amplification bio-replicated skin. All of the test skins are strongly pasted to test model, and drag reduction experiments are conducted according to the rules for vacuole water tunnel test (Q/702J0301-2008). The water temperature is set 28°C and test system degas for more than 1 h before testing.

Taking the smooth surface as reference skin, drag reduction ratio of other bio-replicated skins are shown in Figure 10. It is obvious that optimal drag reduction velocity region can be adjusted by *LsEp* amplification bio-replication, i.e., the peak of drag reduction ratio translational moves by control of bio-replication amplification. Especially, all the peaks of drag reduction remain identical, about 11%, which agree well with our previous studies. The adjustability of drag reduction peak indicates *LsEp* amplification bio-replication can adjust excellent drag reduction of nature surface from living environment to various industrial environments.

CONCLUSION

LsEp amplification bio-replication approach was proposed to adjust optimal velocity region of shark skin by taking use of solvent-swelling PDMS as replica mold. The swelling ratio and swelling rate of PDMS immersed in gaseous *n*-hexane were made clear by various experiments. Apart from controllability of PDMS swelling, higher accuracy even up to 95% was achieved by comparison between real shark skin, first-time and second-time bio-replicated shark skins. Especially, swollen volume was proved to about 34% by just one time amplification, and increase at

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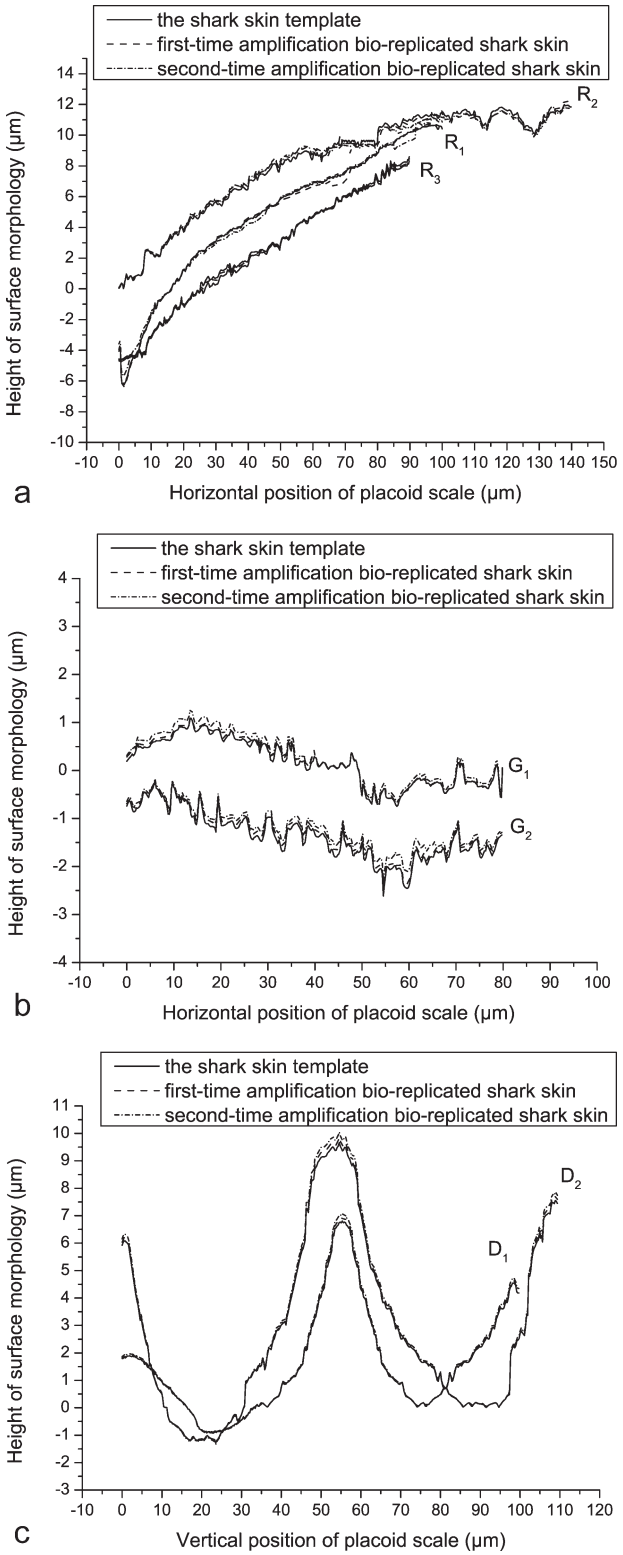

Figure 9. The surface curves of the real shark skin and its corresponding amplified replication which has been zoomed out 1.34 and 1.80 times. The curve is located at (a) $R_{i(i\ =\ 1,2,3)}$, (b) $G_{i(i\ =\ 1,\ 2)}$, and (c) $D_{i(i\ =\ 1,2)}$.

secondary exponent with amplification times. Moreover, the maximum drag reduction of large-proportional amplification bio-replicated shark skin was kept identical to real shark skin except

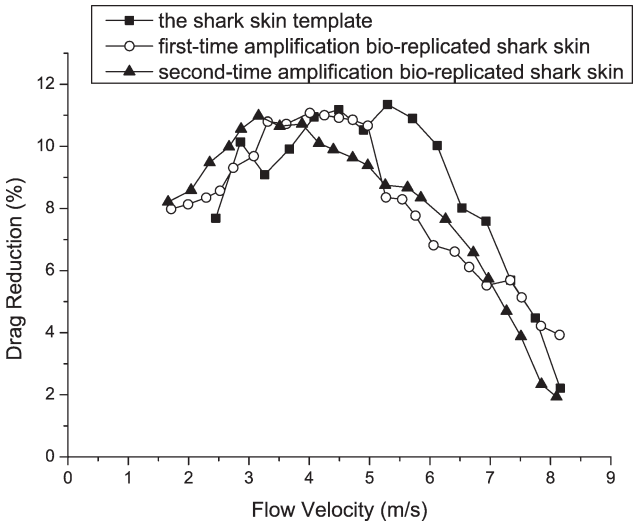

Figure 10. Drag reduction test.

of translation of its optimal velocity region, which indicates that the excellent function of natural function surface can be adjusted to meet various industrial ambient conditions via proposed large-proportional amplification bio-replication.

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REFERENCES

1. Bechert, D.; Bruse, M.; Hage, W.; Van Der Hoeven, J.; Hoppe, G.; *J. Fluid Mech.* **1997**, *338*, 59.
2. Singh, R. P. *Drag Reduction.* Encyclopedia Of Polymer Science and Technology, **2004**.
3. Shan, H. Y.; Zhou, H.; Sun, N.; Ren, L. Q.; Chen, L.; Li, X. Z. *J. Mater. Process. Technol.*, **2008**, *199*, 221.
4. Cheng, H. B.; Feng, Y. P.; Ren, L. Q.; Suet, T.; Wang Y. T. *J. Mater. Process. Technol.*, **2009**, *209*, 4563.
5. Dean, B.; Bhushan, B. *Phil. Trans. Soc. A* **2010**, *368*, 4775.
6. Walsh, M. J. *AIAA J.* **1983**, 21.
7. Choi, H.; Moin, P.; Kim, J. *J. Fluid Mech.* **1993**, *255*, 503.
8. Bechert, D.; Hoppe, G.; Reif, W. E. *On the Drag Reduction of the Shark Skin,* AIAA Shear Flow Control Conference, **1985**.
9. Viswanath, P. *Prog. Aerospace Sci.* **2002**, *38*, 571.
10. Büttner, C.; Schulz, U. *Smart Mater. Struct.* **2011**, *20*, 094016.
11. Han, X.; Zhang, D.; Li, X.; Li, Y. *Chinese Sci. Bull.* **2008**, *53*, 1587.
12. Han, X.; Zhang, D. Y.; *Sci. China Ser. E: Technol. Sci.* **2008**, *51*, 890.
13. Zhang, D. Y.; Li, Y. Y.; Han, X.; Li, X.; Chen, H. W. *Chinese Sci. Bull.* **2011**, *56*, 938.

14. Oeffner, J.; Lauder, G. V. *J. Exp. Biol.* **2012**, *215*, 785.
15. Abduallah, A. B. E.; Mallon, P. E. *J. Appl. Polym. Sci.* **2010**, *115*, 1518.
16. Jakubinek, M. B.; Whitman, C. A.; White, M. A. *J. Thermal Anal. Calorim.* **2010**, *99*, 165.
17. Roy, R.; Agrawal, D. K.; McKinstry, H. A. *Annu. Rev. Mater. Sci.* **1989**, *19*, 59.
18. Shim, W. S.; Yoo, J. S.; Bae, Y. H.; Lee, D. S. *Biomacromolecules* **2005**, *6*, 2930.
19. Friedrich, T.; Tieke, B.; Stadler, F. J.; Bailly, C. *Langmuir* **2011**, *27*, 2997.
20. Gui, X. C.; Cao, A. Y.; Wei, J. Q.; Li, H. B.; Jia, Y., Li, Z., Fan, L. L.; Wang, K. L.; Zhu, H. W.; Wu, D. H. *ACS Nano* **2010**, *4*, 2320.
21. Mabilleau, G.; Basle, M. F.; Chappard, D. *Langmuir* **2006**, *22*, 4843.
22. Shin, M.-S.; Kim, S. J.; Kim, I. Y.; Kim, N. G.; Song, C. G.; Kim, S. I. *J. Appl. Polym. Sci.* **2002**, *85*, 957.
23. Venkatraman, S.; Nixon, A.; Highe, A. *J. Appl. Polym. Sci.* **1994**, *52*, 1619.
24. Sonmez, H. B.; Karadag, K.; Onaran, G. *J. Appl. Polym. Sci.* **2011**, *122*, 1182.
25. Vilaplana, F.; Osorio-Galindo, M.; Iborra-Clar, A.; Alcaina-Miranda, M. I.; Ribes-Greus, A. *J. Appl. Polym. Sci.* **2004**, *93*, 1384.
26. Davis, D. S. Nomographs; Chemical Publishing Company: New York, **1960**.
27. Nwaogu, U.; Tiedje, N.; Hansen, H. *J. Mater. Process. Technol.* **2012**.