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Study on the micro-replication of shark skin

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Direct replication of creatural scarfskins to form biomimetic surfaces with relatively vivid morphology is a new attempt of the bio-replicated forming technology at animal body. Taking shark skins as the replication templates, and the micro-embossing and micro-molding as the material forming methods, the micro-replicating technology of the outward morphology on shark skins was demonstrated. The preliminary analysis on replication precision indicates that the bio-replicated forming technology can replicate the outward morphology of the shark scales with good precision, which validates the application of the bio-replicated forming technology in the direct morphology replication of the firm creatural scarfskins.

shark skin, biomimetic surface, bio-replicated forming, micro-replication

Diverse body shapes of creatures provide mankind with abundant configuration resources. The metallization of microorganism with regular shapes has been investigated in the preceding research[1, 2]. In order to extend the application fields of the bio-replicated forming technology, the direct replication of creatural scarfskins to form biomimetic surfaces with relatively vivid morphology is explored in this paper. Being well-known for the "shark-skin effect", shark skins provide us with perfect drag-reducing surfaces[3]. By simplifying and magnifying the shark scales, many investigations have fabricated some kinds of biomimetic shark skins[4–6]. Whereas, the forming of biomimetic shark skins with surface morphology close to the biological prototype is still to be solved[7–9]. In this paper, the bio-replicated forming technology was used to replicate the microscopic morphology of shark skins so as to explore a new fabrication approach of biomimetic surfaces.

1 Materials and methods

Figure 1 shows the process flowsheet of the morphology replication of shark skins.

The basic process is the followings. Firstly, pretreat the sampled shark skins and get the biological templates for the bio-replicated forming technology. Secondly, take micro-embossing and

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micro-molding as two types of material forming methods and get the micro-replication molds. Finally, replicate the molds by polymer casting and get the biomimetic morphology based on shark skins. Additionally, the commonly used replication technologies are only fit for the objects with obtuse bevel angle[10], while shark scales are slantwise cuneiform, which raises new requirements on material liquidity and demoulding.

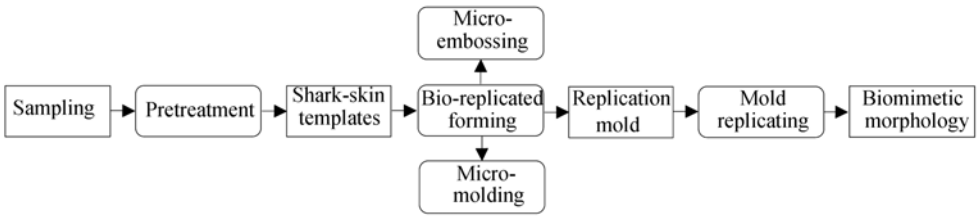

Figure 1 Process flowsheet of the morphology replication of shark skins.

1.1 Templates pretreatment

The templates pretreatment includes cleaning, chemical fixation, re-cleaning, dehydration and desiccation, the purpose of which is to hold the biological prototype and enhance the mechanical strength. The templates used in this paper were sampled from market-sold *Carcharhinus brachyurous* (1.4 m in length). First, cut out two sheets of fresh shark skins (50 mm×50 mm in size) from the symmetrical positions and remove the subcutaneous tissues; second, wash the skins with distilled water and store them at 4℃ for 6 h in glutaraldehyde liquor (2.5% in concentration); third, swash the skins with phosphate buffer solution and place them into aqueous ethanol solution for dehydration; finally, dried at 60℃,the shark-skin templates were got. To prevent the skins from shrinking and warping, a flat plate with certain weight should be pressed on them during the processes above.

Figure 2(a) shows the surface morphology of the skin template. It can be seen that shark skins are covered with diamond-arranged *Placoid scales*, on which there are fine longitudinal grooves (nearly 50 μm in width). *Placoid scales* differ from those of bony fishes both in structure and material[11, 12]: they do not increase in size as the fish grows, so it can be regarded that the scales from the same part of a skin have the same groove structure. Furthermore, *Placoid scales* are made of enamel, and they consist of sharp spines and a rectangular base plate which is deeply embedded in the skin, so the spines and the base plate build a firm cantilever beam, as shown in Figure 2(b).

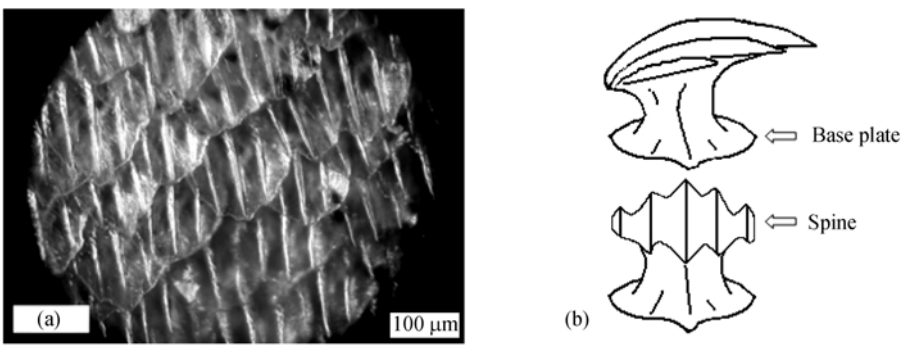

Figure 2 Surface morphology of the shark skin and the structure of a single scale. (a) is the optical micrograph of the shark-skin template; (b) is the illustration of a single shark scale.

1.2 Micro-replicating technology of shark skins

1.2.1 Micro-embossing method. As is illustrated in Figure 3(a), the micro-embossing method involves four steps: substrate heating, templates stacking and isostatic pressing, flexibility demoulding, and mold replicating.

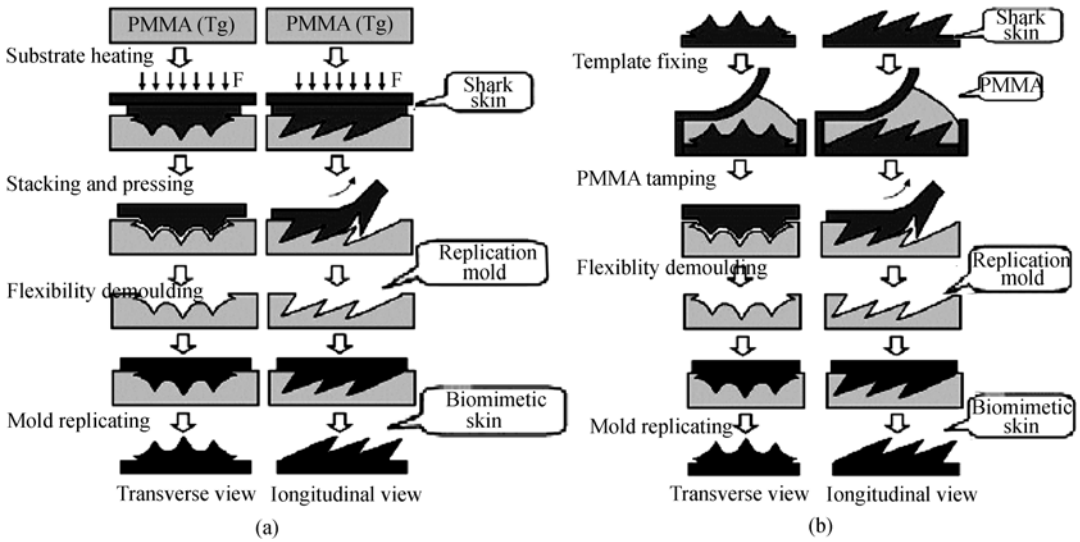

Figure 3 Illustrations of the micro-replicating technology based on shark skins. (a) is the micro-embossing method; (b) is the micro-molding method.

A flat polymethyl methacrylate (abbr. PMMA) plate (80 mm×80 mm×5 mm in size) was selected as the substrate. First of all, the PMMA plate was heated up to its glass temperature (Tg) 105°C, and then the skin template was stacked on it with its scale side adown. Secondly, according to the area of the template, isostatic pressure was applied on the template for 30 min. Thirdly, decrease the temperature to 70℃ slowly with the pressure maintained, then demould, thus the micro-replication mold was gained, as shown in Figure 4(a). Finally, room temperature vulcanization silicon rubber RTV-II 5230 was selected as the replica material. The pre-polymer and curing agent were mixed in a mass ratio of 1000:1 and degassed in a desiccator, then the mixture was poured onto the mold surface and degassed again. After curing and demoulding, the biomimetic shark skin was obtained, as shown in Figure 4(b).

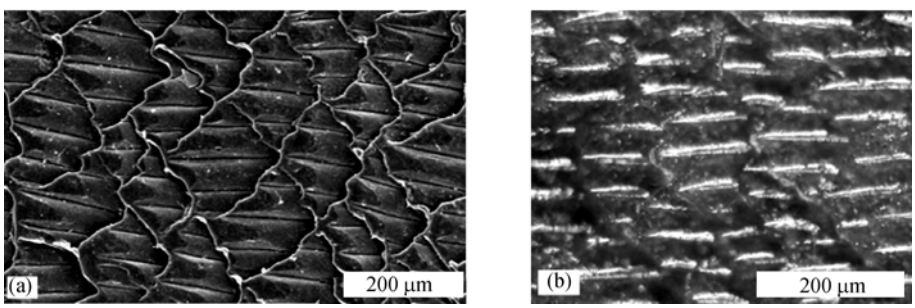

Figure 4 Illustrations of the replicated mold and shark skin made by micro-embossing method. (a) is the SEM photograph of the micro-embossed mold; (b) is the optical micrograph of the biomimetic shark skin.

It can be seen from Figure 4 that relied on the slight liquidity of PMMA at Tg, a little PMMA seeps underneath the scale spines, which ensures the biomimetic shark scales to be detached. Nevertheless, the seeped PMMA will inevitably obstruct the demoulding, thus the control of demoulding order and direction are the key issues. As is shown in Figure 3(a), the scale root and the opposite direction of the scale should be taken respectively as the starting point and the demoulding direction. Depending on the draft angle formed by the scale tip and the elasticity of shark scales as well as the fastness of shark skin, the shark scales can bend both in transverse and longitudinal directions. Therefore, the flexibility demoulding is feasible. The demoulding of the biomimetic shark skin is alike.

1.2.2 Micro-molding method. As is shown in Figure 3(b), the process of the micro-molding method is similar to that of the micro-embossing method except that it directly tamps the uncured polymer onto the shark skins to form the micro-replication mold.

This method requires that the shrinkage rate of the polymer used as the mold material should be low, and that the polymer should be suitable for demoulding. Dental base acrylic resin powder (PMMA homopolymerization powder and evocating agent BPO) and dental base acrylic resin liquid (MMA and crosslinking agent) were used as the two-component material, which generates the noncrystalline polymer PMMA in chain polymerization reaction. The shrinkage rate of PMMA is 0.2%—0.6%[13], which contributes to the size precision of the mold forming. Besides, a dough period will emerge in the curing process of PMMA[14], during which almost no viscosity can be feeled when tamped onto the motherboard. Two components were mixed in a mass ratio of 2:1 and degassed in a vacuum desiccator. During the dough period, the pre-polymer was tamped onto the shark skin by virtue of a flat plate, so that it could fill the gaps fully. After curing, flexibility demoulding and RTV-II 5230 casting, the micro-replication mold and the biomimetic shark skin were fabricated, as shown in Figure 5(a) and (b).

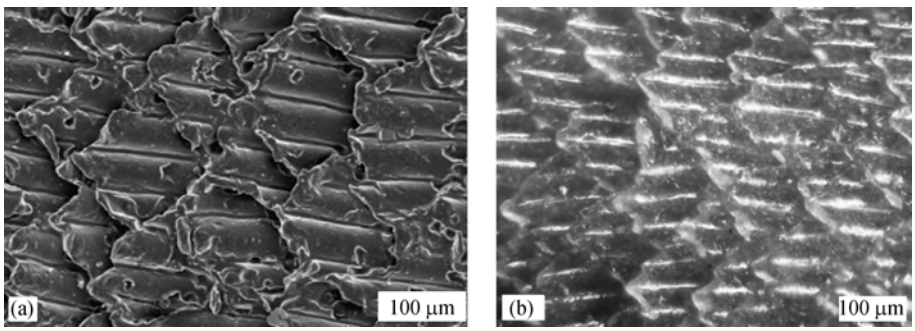

Figure 5 Illustrations of the replicated mold and shark skin made by micro-molding method. (a) is the SEM photograph of the micro-molded mold; (b) is the optical micrograph of the biomimetic shark skin.

2 Results and analysis

The groove shape and the obliquity of shark scales were taken as the evaluating indexes of the replication precision. A stylus profilometer, Ultra Surface (Taylor Hobson Ltd.), was used for the three-dimensional (3D) scanning and imaging of the shark-skin template and the two micro-replication molds. Figures 6 and 7 show the 3D grooves and the corresponding section profiles collected from a single shark scale and two single scale molds.

As to the selection of scanning areas, although a single scale mold is supposed to be compared

with its counterpart template, it will bring much difficulty to sampling. Considering that the structure of *Placoid scales* only lies on their location and species, the scales from the same part of a shark skin approximately have the same structure[11,12]. Therefore, the randomly sampled shark scale and scale mold from the same part are technically comparable.

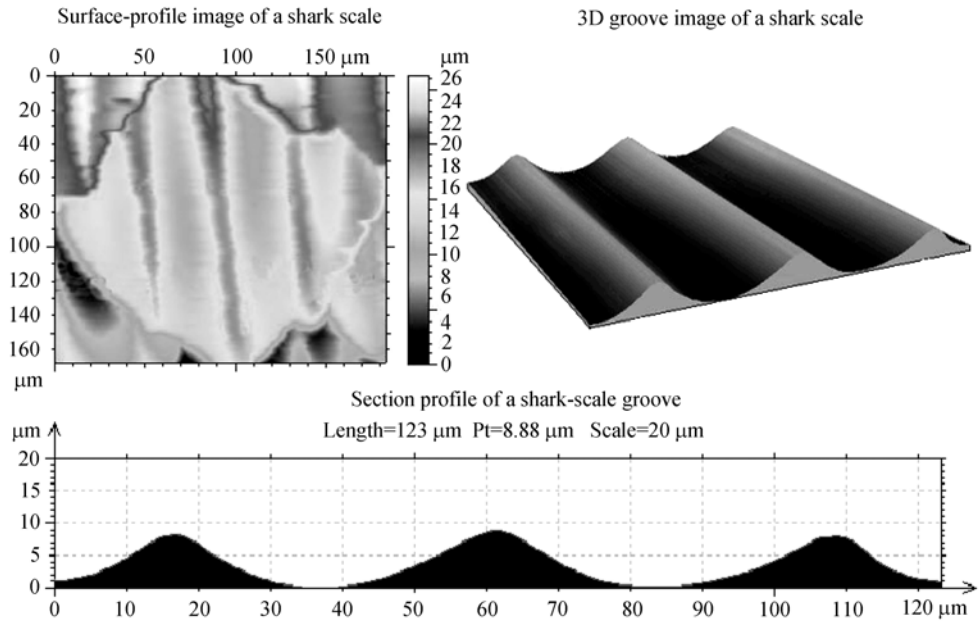

Figure 6 Surface profile imaging of a shark scale.

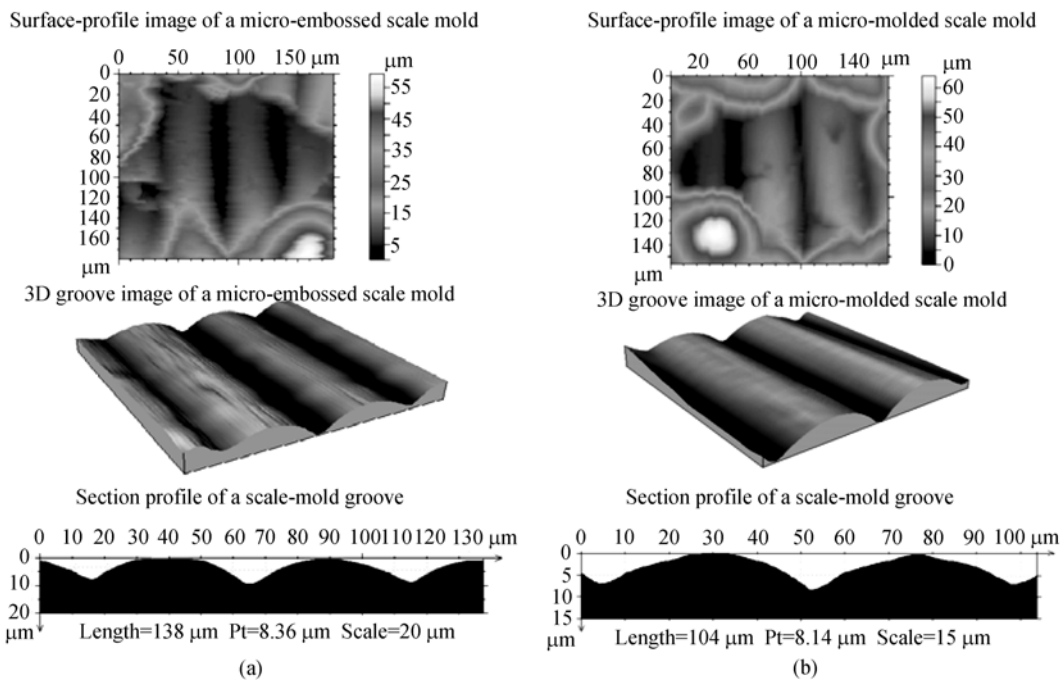

Figure 7 Surface profile imaging of a shark-scale mold. (a) is sampled from the micro-embossed mold; (b) is sampled from the micro-molded mold.

In the replication precision of the scale grooves, because the groove width and spine height are the key parameters of the section profile, the average groove width s and central spine height h extracted respectively from Figure 6 and 7 were compared, as shown in Table 1. It can be seen that compared with the biological template, the groove widths of the two types of molds increased by 5.5% and 2.2%, respectively, and the heights of the central spines decreased by 5.9% and 8.3%, respectively. This shows that the pressure in the micro-embossing process extends the scale groove in transverse, whereas the scale groove almost keeps invariable in the no-pressure micro-molding process. On the other hand, the intervention of pressure ensures the mold pre-polymer to fill in the groove bottom fully. Therefore, the micro-embossing method is preferable to the micro-molding method in the replication of scale spines.

Table 1 Replication-precision comparison of scale groove between the two methods

Mold	Average groove width s (μm)	Central spine height h (μm)	Deformation amount of s Δs (%)	Deformation amount of h Δh(%)
Micro-embossed mold	48.0	8.36	+5.5	–5.9
Micro-molded mold	46.5	8.14	+2.2	–8.3

As to biological templates, s = 45.5 μm, h = 8.88 μm.

In the replication precision of the scale obliquity, the obliquity is the key parameter to determine the hierarchy and independency of shark scales. Figure 8 illustrates the deformation of scale obliquity in the forming of the micro-replication molds: scale tip bends from D' to D and forms a cavity between C and D. In this paper, as to the two molds in Figure 7, taking B as the starting point, a length of 100 μm was scanned along CA direction. As to the biological template in Figure 6, a same length from scale root to tip was scanned as well. Then, the end point of each scanning was taken as the coordinate origin and three profile curves were stacked in Figure 9. Based on the stacked curves, the height offsets ξ and δ of each mold with respect to the template were obtained as shown in Figure 9(b). It can be seen that the deformations of scale obliquity on the two molds increased gradually from the middle part and reached the maximum values 3.8 μm and 8.2 μm at scale tips, which decreased by 13.7% and 27.5%, respectively, compared with the template. This suggests that the micro-molding method has higher precision in the replication of scale obliquity than the micro-embossing method.

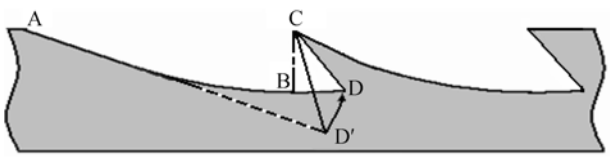

Figure 8 Illustration of the deformation of scale obliquity.

The Comprehensive analysis above indicates that there was no significant difference in the replication precision of the scale grooves between the two methods, and that the micro-molding method is preferred to the other one on the replication of the scale obliquity. Yet the micro-embossing method has certain advantages on the surface integrity over the micro-replication mold.

3 Conclusions

Shark skin has appropriate mechanical strength and heat tolerance, which makes it suitable to be

taken as the replication template of the micro-embossing and micro-molding methods. The analysis on the replication precision validates that the bio-replicated forming technology can be applied to the direct morphology replication of the firm creatural scarfskins.

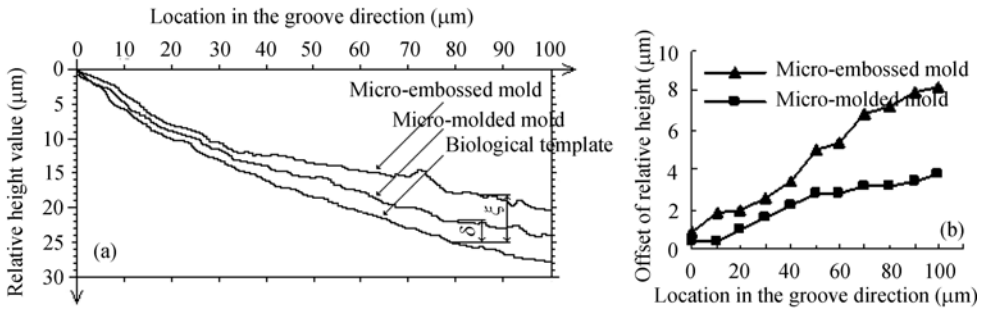

Figure 9 Comparison of the two micro-replication molds in the precision of scale obliquity. (a) shows the stacked profile curves; (b) shows the offset curves of ξ and δ respectively.

Compared with the micro-embossing method, the micro-molding method has higher precision in the morphology replication of creatural scarfskins in general.

As a matter of fact, this paper merely discussed the micro-replicating technology of the outward morphology on shark skins. The material permeability, mechanical strength and other aspects concerned still need to be investigated integratedly. Besides, the improvement of the surface integrity of the micro-molded mold, the measurement of the cantilever length of shark scales also need to be solved in the further research.

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