Imprint Process with In-plane Compression Method for Bio-functional Surface

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In this research, we propose an in-plane compression imprint method as a further development of the special micro patterning method to realize various biomimetic functional surfaces. Biomimetic is popular in the field of engineering in recent years. We focused on biomimetic functional surfaces of natural organisms. For example, micro scales on the wing of a morpho butterfly develop a bright blue color. The scales have specific dendrite-like nano-structures. We aim to mimic such functional surfaces by nano imprint lithography (NIL). NIL has high resolution and high productivity, and is known as a technology that can be applied to various materials. Conventional NIL requires mold release in the process, so it is difficult to form special shapes such as the overhang shape. To solve this problem, we propose an in-plane compression process. In our new process, work materials were imprinted on a stretched silicone film, and imprinted materials were compressed by in-plane compressive stress due to the elastic recovery of the silicone film. In this paper, we show some examples increasing the aspect ratio more than twice by the proposed process. We also show a strategy to form a complicated morpho’s surface pattern with an overhang structure having a high aspect ratio.

Keywords: Nano imprint lithography, Ceramic, In-plane Compression, Hierarchical structure

1. Introduction

Biomimetic is a popular field in the field of engineering in recent years. Many biomimetic researches have been reported to mimic the superior functions of organisms and incorporate them into engineering.

We focused on biomimetic functional surfaces of natural organisms. For example, the micro scales on the wing of a morpho butterfly have specific dendrite-like nano-structures. This structure makes it possible for the morpho butterfly wing to develop a bright blue color. Another example is a super-hydrophobic surface on a lotus leaf. By imitating the surface microstructures of these living organisms, we can control the wettability, friction, and optical properties of the surface of engineering products [1-4]. These properties depend not only on the material but also micro- or nano- structures, so fabrication process for fine patterning should be developed to obtain complicated natural surface structures.

One of candidate processes for the fine surface fabrication is nano imprint lithography (NIL). It has high resolution and high productivity, and is known as a technology that can be applied to various materials [5-7]. In this study we employed thermal NIL process, in which a mold pattern is transferred to the surface of a work material by pressing the heated sample. As it is a simple process but results in excellent resolution, there have been many applications in various fields. For example, imprinted micro patterns are used to control optical polarization and water wettability on resin materials [8,9].

NIL is generally used for organic polymer materials. Micro powder imprint (μPI) process has been proposed and developed to apply the imprint
technique for inorganic materials, such as ceramics and glasses [10-12]. In this process, inorganic nano powders are mixed with polymer binder material to form a compound sheet material. The sheet is imprinted to transfer a fine mold pattern on its surface. Subsequently, the sheet is heated to remove the polymer binder and to sinter. Finally, a dense inorganic sheet with a fine pattern is obtained.

The μPI process could be used to layered materials [13-22]. We call this process with layered material “lamination imprinting”. In lamination imprinting, a laminated material, in which different materials are stacked, is used as a work material. Of course, the surface pattern could be formed into the same pattern with a mold. Also, the interfaces of the laminated material could be formed simultaneously. It is noted that the interface pattern would be different from the mold pattern. The interface pattern is determined by process conditions, such as pressing speed, initial thickness of each layer, and mechanical properties of the materials.

As further development of NIL, we aim to higher aspect ratio pattern and more variation of the pattern shape. Conventional NIL requires mold release in the process, so it is difficult to form some shapes such as the overhang shape found in the micro scales of morpho butterflies. We propose a new process to add processing in the in-plane direction to NIL, which generally performs processing only in the vertical direction.

Figure 1 shows an outline of the imprint method with the in-plane compression. First, imprint processing is performed on a stretched silicone film. Next, the stretched silicone film is recovered at a low speed, and the imprinted body on the silicone film is compressed by the in-plane compressive stress. By processing in the in-plane direction, various shape evolution could be expected, such as an overhang shape and multi-layered structure. If processing of these special shapes using NIL is realized, it can be expected to provide high functionality to the object surface at low cost.

2. Experimental

Alumina compound sheet was selected in this experiment. The outline of the experiment is shown in Fig. 2. First, the silicone film was stretched and fixed to the substrate. Next, a lamination sheet of alumina sheets was prepared as a work material and fixed on the stretched silicone film.

The starting alumina compound sheet was mixture of alumina nano powder and aqueous polymer resin based on polyvinyl alcohol (PVA). Alumina is a structural material with high hardness, excellent insulation and heat resistance, and is used in most industrial products as fine ceramics. Alumina compound sheets were prepared using the doctor blade method. The prepared alumina sheets were stacked into one laminated compound sheet. A thin black tracer layer was sandwiched between the layers for easy observation of the interface.

The average particle size of the alumina powder (TM-DAR, Taimei Chemical Co., Ltd.) used in the experiment was 0.1 μm and the purity was 99.99%. Polyvinyl alcohol (degree of polymerization of 500, Wako Pure Chemical Industries, Ltd.) was used as a binder for the compound sheet, and glycerin (Wako Pure Chemical Industries, Ltd.) was used as a plasticizer. Polyvinyl alcohol is a thermosetting resin and suitable for imprinting. Glycerin is generally used as a plasticizer for polyvinyl alcohol, and it was used to improve the formability of the alumina compound sheet in this study.

These materials were mixed with pure water to make an alumina compound sheet slurry. This slurry contained alumina powder, PVA and glycerin at 43:30:27 vol%. The prepared slurry was formed into a sheet of uniform thickness on a silicone film using a doctor blade method. The water was removed by heating the formed slurry at a temperature of 80 °C for 600 s using an oven to obtain a compound sheet. Next, apply a tracer layer on the alumina compound
sheet using a brush. As a tracer layer, carbon black dispersed aqueous solution (Aqua-Black 162, Tokai Carbon Co., Ltd.) was used. This dispersed solution was used after diluting it 40 times to obtain better compatibility to the alumina compound sheet. After applying the tracer layer, the alumina slurry was applied again using the doctor blade method, and the same drying procedure was performed. Figure 3 shows a cross-sectional view of the fabricated laminate. The white part shows the alumina compound sheet and the black line shows the tracer layer. The thickness of the laminated layers were 20 μm in the upper layer and 100 μm in the lower layer, respectively.

The prepared laminated sheet was imprinted using a polyimide mold shown in Fig. 4. The mold pattern was a corrugated line and space shape with a pattern depth of 46 μm and a pitch of 150 μm. Before imprint, the laminated sheet was set in a chamber in which temperature 30 °C was and humidity was 70 % for 1 h (3.6 ks) to obtain better formability. The imprint pressure was 7.5 MPa, and the imprint temperature was 80 °C.

After imprinting, the imprinted sheet was in-plane compressed by recovering the silicone film at a low speed. As the elastic recovery force of the silicone was less than imprinting force, we added water content in the work sheet. Before in-plane compression processing, the imprinted body was set in a chamber of 80% humidity for 1 h (3.6 ks).

In this study, we changed the in-plane compression ratio by changing the stretch ratio of the silicone film. The compression ratio to the imprinted body was performed under four conditions of 1.0, 1.5, 1.7, and 2.0, and the shapes of the laminated imprint molded body subjected to in-plane compression processing were observed.

3. Results and discussion

Figure 5 shows cross-sectional photographs of the in-plane compression imprinted compound sheets. Figure 5(a) shows an initial state before in-plane compression, and Figs. 5(b-d) show with a compression ratio of 1.5, 1.7, and 2.0, respectively. At first, the imprinted surface pattern and interface shape before in-plane compression show a gentle wavy line and space shapes. The surface pattern was similar to the mold pattern, and the interface pattern showed less...
amplitude.

By in-plane compression, the surface and interface patterns evolved differently. The surface pattern at the valley became a sharp shape, and the sidewalls contacted each other at the 2.0 in-plane compression ratio. The interfacial pattern was gradually folded as in-plane compression, and it became a thin deep pattern, which was a high aspect pattern, finally. The pitch of the in-plane compressed body was shown in Fig. 6. The result show that there was almost no mismatch between the imprinted sheet and the silicone substrate during shrinkage process of the silicone film.

Next, the pattern depth and pattern width of the peaks and valleys of the in-plane compression molded product were measured as shown in Fig. 7. Figure 7(a) shows the measurement points of the surface pattern of the compact, and Fig. 7(b) shows the measurement points of the interface pattern of the compact. The pattern depth and pattern width were defined using the half-width as shown by the white line. The aspect ratio of the peak and valley patterns can be calculated from these values.

Figure 8 shows the aspect ratio of the surface and the interface patterns at the ridges of the in-plane compression molding. No significant change in aspect ratio was observed at the peak of the compact, while the aspect ratio drastically increased at the valleys of the compact. This increase of the aspect ratio was shown particularly in the interface pattern. At the initial state, the aspect ratio of the interface of the valley portion of the compact was 0.15, and it changed into 2.4 at the in-plane compressibility of 2.0, which was about 15 times.

The difference between changes in the aspect ratio of the surface and the interface patterns was caused by folding of the patterns. Both of the surface and the interface were folded during the in-plane compression, but part of the folded surface pattern was embedded into inside of the layer. On the other hand, the interface pattern did not change the length since the both layers constrained from upper and lower sides.

As described above, the interfacial pattern was folded but the length was not changed. This behavior could be useful to fabricate a hierarchical pattern. We propose a process for the hierarchical pattern using our in-plane imprint method. The outline of the process is shown in Fig. 9. First, imprint is performed using a fine pattern mold. Next, a sacrificial layer is applied to protect the first mold pattern. Then, by performing a second-step imprinting using a mold with a rough pattern, a shallow uneven shape is transcribed to the surface of the work sheet. Next, in-plane compression processing is performed to deform the compact so as to fold the interfacial fine pattern. Finally, the sacrificial layer is removed to obtain a compact. By applying the in-plane compression imprint method, it is expected to produce multi-layered structure.
with high aspect ratio. Morpho butterfly’s nano-pattern could be obtained by the proposed method as shown in Fig. 9.

4. Conclusion

We proposed and developed an in-plane compression imprinting method in this work. An additional compression in the in-plane direction was carried out using the elastic recovery of a silicone substrate. The in-plane compression imprint was performed on the laminate material, and we observed the shape evolution of the surface and interface patterns. As a result, the pattern with much higher aspect ratio was obtained. The process could be used for further complicated biomimetic functional surfaces such as Morpho butterfly’s nano-pattern. A computational deformation analysis of imprint process [23] would be a powerful tool to design the pattern.

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