HYBRID FILM FOR SELF-ADHESION AND SHAPE-CONTROLLING

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ABSTRACT

We report a hybrid film that is composed of "polymer nanosheet" with a hundreds-of-nanometer-thick film and "punched film" with hundreds-of-micrometer-thick film. Because of the thickness, the nanosheet is able to adhere to biological tissues without a glue, but is sometimes difficult to handling. Our hybrid film is established both adhesiveness of the nanosheet and shape-controlling ability of the punched film. In this paper, first, we fabricated the cylindrical-shaped hybrid film. Next, we achieved the hybrid film unfold into flat shape. Finally, we evaluated the adhesion force of the hybrid film and confirmed that the hybrid film can adhere to biological tissues.

INTRODUCTION

Nanosheets are hundreds-of-nanometer-thick polymeric film which is made from poly (l-lactic acid) (PLLA) or poly (styrene-butadiene-styrene) (SBS). Because of the self-adhesive ability and biocompatibility, nanosheets are expected to be used as plasters for surgery [1-3]. Recently, biomedical application of the nanosheet for endoscopic surgery was proposed [4]. After injecting from the endoscope, the nanosheet is adhered to a biological tissue. This surgery requires less incision comparing to open surgery. In the endoscopic surgery, the nanosheet should be contained inside the endoscope, unfolded into the original flat shape, and adhered to the biological tissue. However, unfolding the nanosheet into the flat shape is difficult after injecting from the endoscope due to thickness and flexibility of the nanosheet.

In this work, we propose the hybrid film which composed the nanosheet and a double-layered structure (a punched supporting and a stretching layers). The hybrid film

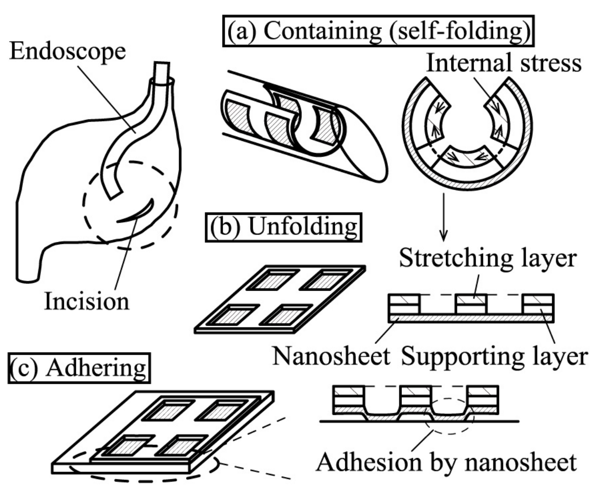

Figure 1: Experimental strategy of sheet-shape changing and adhesion to a biological tissue of the hybrid film in endoscopic surgery. (a) The hybrid film is folded into cylindrical shape by giving internal stress. (b) The hybrid film can be unfolded into flat shape by relieving internal stress. (c) The hybrid film can be adhered to the biological tissue because of the free-standing part of the nanosheet.

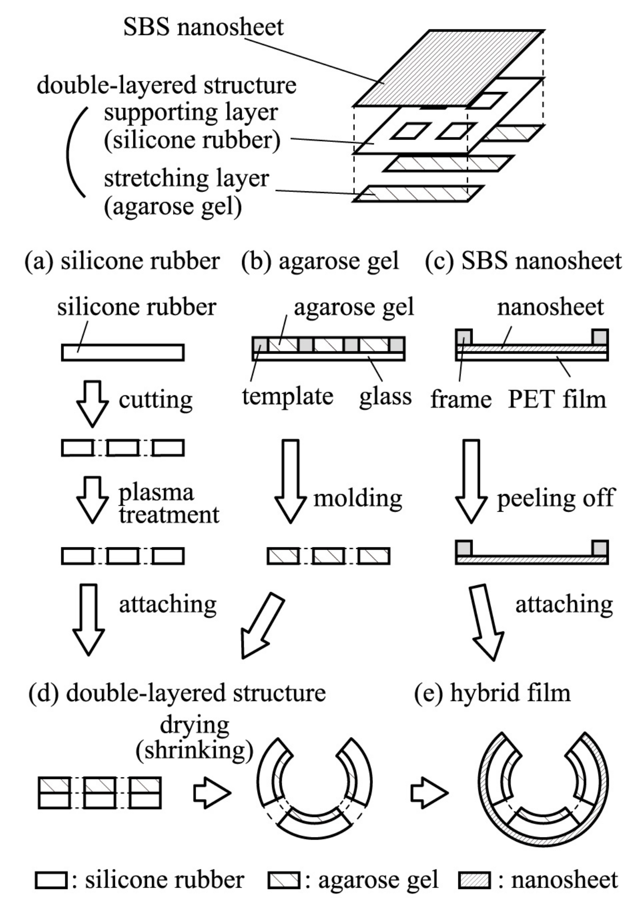

Figure: 2 Fabrication process of the hybrid film. (a) We punched a silicone rubber by cutting. To improve surface adhesiveness, the silicone rubber provided plasma treatment. (b) An agarose gel was fabricated by molding. (c) An SBS nanosheet was fabricated on a PET film. A single layer of the nanosheet was obtained by peeling off from the PET film. Using the framework allowed for facile handling of the nanosheet. (d) The hybrid film was composed of the agarose gel, the silicone rubber, and the nanosheet. And the hybrid film was folded into the cylindrical shape by drying the agarose

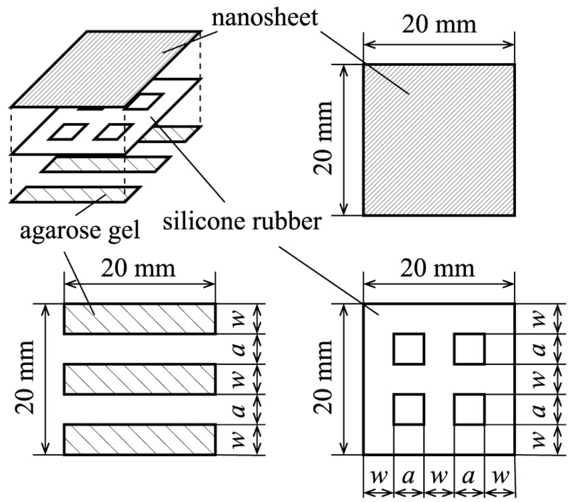

Figure: 3 The design parameter of the hybrid film.

provided the self-folding ability and self-unfolding ability to the nanosheet without losing adhesiveness.

FABRICATION

Fig. 1 shows the schematic image of the hybrid film. First, the hybrid film was folded into cylindrical shape by giving internal stress for containing into the endoscope. Second, the hybrid film was unfolded into a flat shape by relieving internal stress. Finally, the hybrid film was adhered to a biological tissue thanks to the adhesiveness of free-standing SBS nanosheets.

For fabricating the hybrid film, we used a triple-layered structure, composed of a SBS nanosheet and a double-layered structure (a punched supporting and a stretching layer). The hybrid film was folded into cylindrical shape owing to the internal stress of the stretching layer. Fig. 2 shows fabrication process and structure of the hybrid film. We used a silicone rubber for the punched supporting layer because it can control mechanical property. We also used an agarose gel for the stretching layer because the agarose gel can change the volume greatly by drying.

First, the silicone rubber was punched by cutting. And, the agarose gel was fabricated by molding. By changing the shape of a template, we controlled the shape of the agarose gel. Furthermore, the SBS nanosheet was fabricated on a PET film [2]. The SBS is dissolved in tetrahydrofuran (THF), and the nanohseet is fabricated by coating THF on the PET film and drying. The single layer of the SBS nanosheet was obtained by peeling off from the PET film. At that time, we handled the nanosheet easily by framing. Second, we fabricated the double-layered structure by piling up the silicone rubber and the agarose gel, and the silicone rubber was provided plasma treatment to improve surface adhesion. One day after drying the agarose gel, the double-layered structure was spontaneously folded into the cylindrical shape by shrinking of the agarose gel. Finally, we obtained the hybrid film by attaching the nanosheet to the top of the double-layered structure. In fabricating the hybrid film, we made the nanosheet and the double-layered structure separately because the nanosheet was broken during drying. Then, the hybrid film was unfolded into the flat shape due to swelling of the agarose gel in water. And the hybrid film can be transferred to the biological tissue.

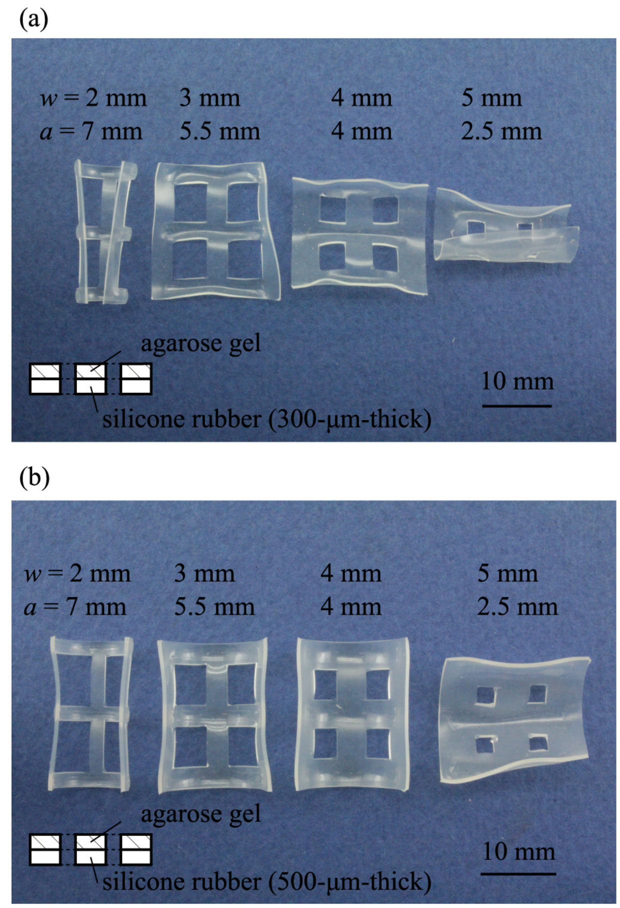

Figure 4: Photographs of the double-layered structure. The width of a silicone rubber w are 2 mm, 3mm, 4 mm, and 5 mm. (a) The double-layered structure which composed of a 300-μm-thick silicone rubber and a 1-mm-thick agarose gel. (b) The double-layered structure which composed of a 500-μm-thick silicone rubber and a 1-mm-thick agarose gel.

EVALUATIONS

We evaluated self-folding ability, self-unfolding ability, and self-adhering ability of the hybrid film. We supposed that the radius of curvature of the hybrid film was depended on the design parameter of the silicone rubber and the agarose gel, and that the adhesion force of the hybrid film was dependent on the area of free-standing part of the nanosheet. For designing the hybrid film, we evaluated the radius of curvature and the adhesion force between the hybrid film and glass substrate.

Self-folding

We fabricated the hybrid film, composed of a

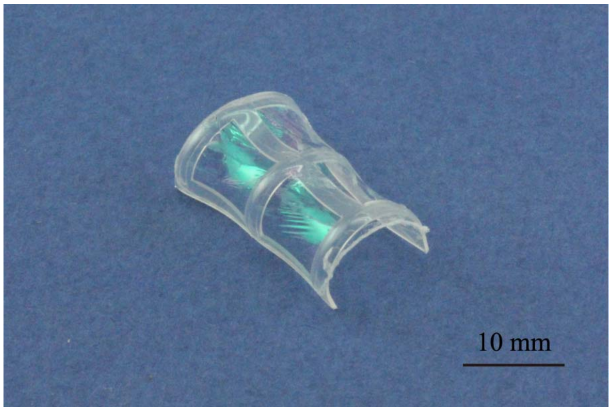

Figure 5: A photograph of the hybrid film, composed of a 610-nm-thick nanosheet, a 300-μm-thick silicone rubber and a 1-mm-thick agarose gel. The radius of curvature was 5.3 mm.

(a) (b)

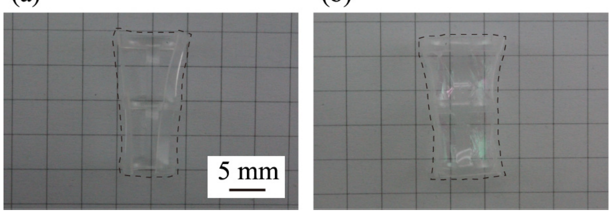

Figure 6: The state of sheet-shape change of the hybrid film (20 mm × 20 mm). (a) A photograph of the double-layered structure observed from upper side. The radius of curvature was 4.9 mm. (b) A photograph of the hybrid film observed from upper side. The radius of curvature was 5.3 mm.

610-nm-thick nanosheet, a 300-μm-thick or 500-μm-thick silicone rubber and a 1-mm-thick agarose gel ([Agarose]=1 wt%), where the nanosheet was made from SBS.

First, we evaluated self-folding ability of the double-layered structure. Fig. 3 shows the design parameter of the hybrid film. Fig. 4(a) shows the double-layered structure, composed of a 300-μm-thick silicone rubber and a 1-mm-thick agarose gel. In case that the width of silicone rubber *w* was 2 mm, the radius of curvature of the double-layered structure was 4.7 mm. However, the double-layered structure was folded from the other side in case that the width of silicone rubber *w* were 4 mm, and 5 mm. And Fig. 4(b) shows the double-layered structure, composed of a 500-μm-thick silicone rubber and a 1-mm-thick agarose gel. In case that the width of silicone rubber *w* was 2 mm, the radius of curvature of the double-layered structure was 5.4 mm. The double-layered structure was folded from the other side in case that the width of silicone rubber *w* was 5 mm. In previous research, the way of rolling (long-side rolling or short-side rolling) was changed by the aspect ratio of the rectangular [5]. We confirmed that the width and mechanical character (thickness and Young's modulus) of silicone rubber was important for designing the radius of curvature and the way of the rolling.

(a) (b)

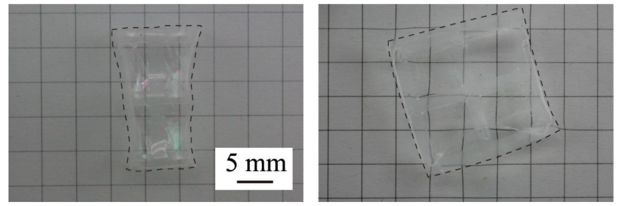

Figure 7: The state of sheet-shape change of the hybrid film (20 mm × 20 mm). The cylindrical-shaped hybrid film was unfolded into a flat shape. (a) Initial state observed from upper side. The radius of curvature was 5.3 mm. (b) After soaking in pure water, the hybrid film was unfold into a flat shape. The radius of curvature was 37.6 mm.

And we confirmed that the radius of curvature of the double layered structure would be tunable by controlling the mechanical character of the silicone rubber. From Fig. 4, we decided to design the width of silicone rubber *w* to be 2 mm.

Next, we fabricated the hybrid film, composed of a 610-nm-thick nanosheet, a 300-μm-thick silicone rubber and a 1-mm-thick agarose gel (Fig. 5). The width of the silicone rubber *w* was 2 mm. Though the radius of curvature of the double layered structure was 4.9 mm (Fig. 6(a)), the radius of curvature of the hybrid film became 5.3 mm (Fig. 6(b)), due to the internal stress of the nanosheet. Any other nanohseet, for example PLLA nanohseet etc., can be fabricated the hybrid film if the nanosheet can adhere to the silicone rubber.

Self-unfolding

We evaluated self-unfolding ability of the hybrid film. Fig. 7 shows the shape transformation of the hybrid film. We soak the hybrid film into pure water. After seaking into pure water, the radius of curvature changed from 5.3 mm to 37.6 mm. As shown in Fig. 7(b), the cylindrical-shaped hybrid film was unfolded into the flat shape by swelling of agarose gel and shape stability of the silicone rubber. The time of unfolding was less than 1 minute. In addition, we could succeeded to change the time of unfolding by controlling the thickness of agarose gel and flexural rigidity of silicone rubber.

Self-adhering

After soaking the hybrid film into pure water, the hybrid film was unfolded into flat shape. And we placed the hybrid film on human skin. From Fig. 8, we confirmed that the hybrid film was adhered to skin after recovering the original flat shape. We also evaluated the adhesiveness of the hybrid film by changing the size of a hole ($a \times a$ [mm^2]). We connected the hybrid film to a hand-made apparatus using a double-sided tape, and measured peeling force between hybrid films and glass substrates (Fig. 9(a)). For evaluation, we used a hybrid film with a 610-nm-thick nanosheet and a 25-μm-thick polyimide. Fig. 9(b) shows the relationship between the adhesion force F and the exposed area ratio α (the ratio between the area of the free-standing nanosheet and

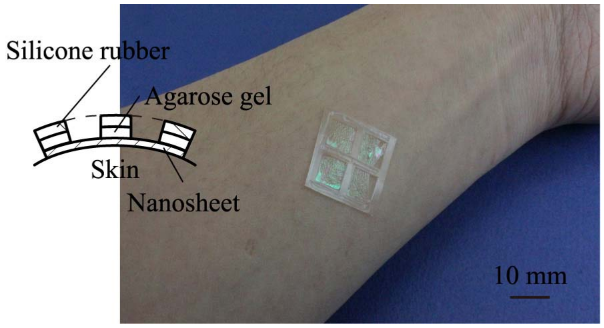

Figure 8: The hybrid film can adhere to the skin after unfolding into a flat shape.

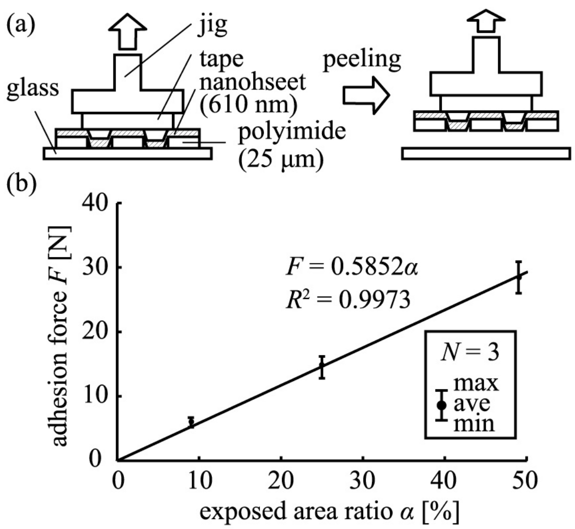

Figure 9: (a) Schematic image of measuring the adhesion force F. (b) The relationship between the adhesion force F and the exposed area ratio α (the ratio between the area of free-standing nanosheet and the area of the hybrid film (10 mm × 10 mm)).

the area of the hybrid film). From Fig. 9(b), the adhesion force F was proportional to the exposed area ratio α. This result indicates that we can design the adhesion force F by changing the area of the “free-standing” nanosheet.

CONCLUSIONS

In conclusion, we achieved the hybrid film which can be unfolded into the flat shape from cylindrical shape to be adhered. We fabricated the hybrid film, composed of a 610-nm-thick SBS nanosheet and a double-layered structure (a 300-μm-thick silicone rubber and a 1-mm-thick agarose gel). First, we evaluate the self-folding ability. We obtained the cylindrical hybrid film whose radius of curvature is 5.3 mm. Second, we evaluate the self-unfolding ability. The cylindrical-shaped hybrid film was unfolded into the flat shape by swelling of agarose gel. The radius of curvature is changed from 6.4 mm to 37.6 mm. Finally, we evaluate the self-adhesion ability. We confirmed that the hybrid film can be adhered to skin after recovering the original flat shape.

ACKNOWLEDGEMENT

This work was partially supported by JSPS KAKENHI Grant Number 26286031 (T.F. and E.I.).

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