Manufacturing of Poly-DL-Lactic Acid Nanosheets and Evaluation of Tribological Characteristics between Nanosheet Surfaces and Fingers

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Abstract

Attention is focused on ultra-thin polymer films (nanosheets) that have high flexibility and adhesiveness and their thickness can be controlled to several tens of nanometers. These nanosheets can be neatly attached to surfaces with complex irregularities without the use of adhesives. Therefore, the ratio of surface area to thickness is very large, and we believe that the relationship with friction is very significant in nanosheet technology for biomedical applications such as wearable devices and wound dressings. The purpose of this study is to investigate the contact mechanism of nanosheets with human fingertip skin in terms of friction coefficient by using the microgravure printing method, which enables thin film coating. From the results of film thickness measurements, it was found that nanosheets of any thickness can be fabricated by the microgravure printing method. The friction measurement results showed that the coefficient of friction of the nanosheets decreased except for vertical loads above F_z*=2N. The coefficient of friction increased as the contact area increased. It was found to increase with increasing vertical load under the immersion in water conditions, and conversely, it decreased under the drying condition except for the high normal load of 2N. Furthermore, the coefficient of friction was found to increase with increasing nanosheet thickness. Observation of wear traces showed that when the vertical load was sufficiently high (*$F_z = 2$ N*), wear traces containing oily traces such as sebum and sweat appeared on the nanosheet surface. This is thought to function as a lubricant. Polymer nanosheets are a new material, and there have been few studies on friction with this material. Research on friction is very important because polymer nanosheets are expected to be applied to wound dressings and displays of electronic devices.*

Keywords: *Nanosheet, Fingertip, Friction, Real contact area, Friction of coefficient.*

1. Introduction

The nanosheets are a nanostructure that has thickness controlled to several tens of nm. Nanosheets have high flexibility and high adhesiveness and have received much attention in recent years. Since nanosheets have a very large surface area relative to their thickness, they can be neatly attached to complex uneven surfaces without adhesives [1][2][3][4]. Therefore, it is expected to be applied to devices such as wearable electronic substrates and wound dressings that are attached to the skin. By making the substrate of the wearable electronic device extremely thin, the size can be reduced without

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changing the original function of the electronic device, and weight reduction and cost reduction can be expected. This makes nanosheets applicable to a wide range of research fields. The nanosheets can be made from a variety of materials, but Okamura et al. [1] produced nanosheets using Poly-L-lactic acid (PLLA), which has characteristics such as biocompatibility and biodegradability, as a material. As a result, they have developed a nanosheet that can be applied inside the living body without causing the human body to cause a rejection reaction. In addition, since the lung repair of animals using nanosheets was carried out by previous research, it is expected to be applied to humans in the future. Therefore, nanosheets are expected to be widely used in the medical field. In nanosheet technology for biomedical applications, the effects of friction and wear on the skin are extremely large as thin-film sensors and wound dressings to be attached to the skin. The frictional properties of the skin are closely related to the condition of the skin. Dry skin has a low coefficient of friction, and moist skin has a high coefficient of friction [5][6]. The change in friction also greatly depends on the texture and softness of the skin. From this, it is very important to know the frictional properties between nanosheets and skin when considering the application to living organisms. Moreover, when predicting the future development of wearable electronic devices, the conventional nanosheet manufacturing method lacks productivity. In the conventional manufacturing method, a spin coating method is used in which the solution is made thin and uniform by the centrifugal force generated by rotating the silicon substrate coated with the solution at high speed. However, the size of the nanosheet that can be manufactured at one time is the area of the substrate. It is not suitable for future demand and supply because it depends on the Silicone substrate size. Kai et al. [7] improved this problem by using a roll-to-roll (R2R) method that can support and convey the film with multiple rollers. This method allows continuous coating, drying, and winding during the transportation process. In addition, the coating process uses a micro-gravure (MG) printing method that allows non-contact coating by rotating a roll with a finely processed surface in the opposite direction to the film being transported [8][9][10]. In the MG printing method, when the solution is scraped up from the solution tank, a liquid pool is generated due to surface tension between the roll and the film. Depending on the amount of liquid pool formed at that time, it is possible to form films of various thickness. PLLA nanosheets were produced using a production method that combined these two methods. Nanosheet coating technology that can be incorporated into the R2R method is indispensable for manufacturing ultra-thin film sensors on production lines.

Therefore, the purpose of this study was to elucidate the tribological characteristics between nanosheets and human skin, and nanosheets with thicknesses of 50, 100, 150, and 200 nm were prepared, and the contact mechanism was investigated from the viewpoint of friction coefficient.

2. Materials and methods

In previous studies, PLLA has been used as a material for poly lactic acid, but it is crystalline, and its physical properties change at high temperatures so the development of processes such as heat treatment cannot be expected. In this study, Poly-DL-Lactic Acid (PDLLA) was used to solve this problem. Since PDLLA has different chemical properties and is amorphous compared to PLLA, nanosheets do not crystallize even when exposed to fire, and their physical properties do not change during molding at high temperatures such as embossing.

Therefore, in this experiment, PDLLA was used as the material for nanosheets, and nanosheets were produced using the MG printing method. Next, the film thickness of the prepared nanosheet was measured, the vertical load and the film thickness were changed, and each frictional force was measured. We also visualized the contact surface between human skin and nanosheets and calculated using image analysis software (Vision Assistant) for the contact area ratio.

2.1. Nanosheet fabrication procedure and method

Figure 1 shows the thin film coating machine used to fabricate nanosheets. Figure 2 shows the procedure of the method applied when producing nanosheets. This method is called the sacrificial film method and is a process in which nanosheets can be peeled off by removing the intermediate layer formed between layers (Silicon substrate and nanosheets). The film thickness was adjusted by changing the solution concentration and circumferential speed ratio with a thin film coating machine using the MG printing method. The circumferential speed ratio can be obtained by dividing the rotation speed of the MG roll by the transport speed of the film. In coating, it requires the solid polymer to be liquefied and placed in a solution tank. From this, the polymer to be used and its solvent are described. First, polyvinyl alcohol (PVA) was used for the intermediate layer. Since PVA is water-soluble, ultrapure water was used as the solvent. At this time, the concentration of the PVA solution dissolved in ultrapure water was 20 mg/ml. Next, PDLLA was used as the material for the nanosheets, and chloroform was used as the solvent. The concentrations of PDLLA dissolved in chloroform were 10 and 20 mg/ml. The film substrate wound in a roll shape was set in the thin film coating machine for unwinding. First, a solution of PVA dissolved in ultrapure water was applied and dried. Next, a solution of PDLLA dissolved in chloroform was applied and dried. The production conditions are shown in Table 1. By immersing the prepared three-layer film (film substrate, PVA, PDLLA) in ultrapure water, the intermediate layer PVA was dissolved and the PDLLA nanosheet was peeled off from the film substrate.

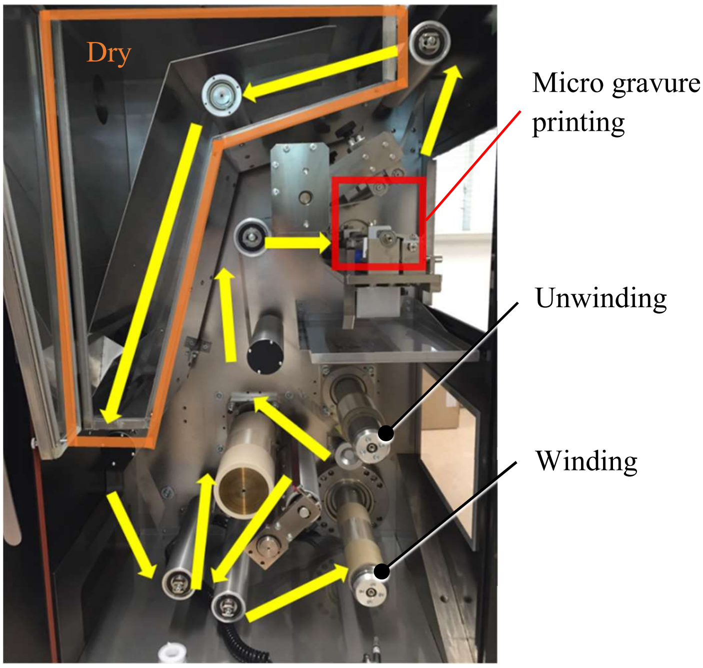


Figure 1. Internal structure of roll-to-roll; This device can continuously unwind, coat, dry, and wind.

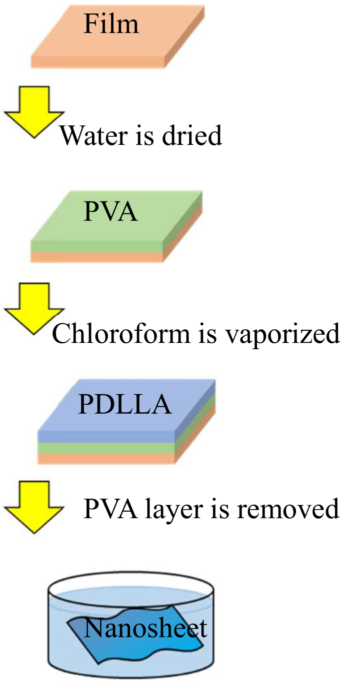


Figure 2. Sacrificial film method

Table 1. Experimental conditions

			PVA	PDLLA
Solvent			Ultrapure water	Chroroform
Solution concentration	S	[mg/ml]	10	10, 20
Conveying speed	V_f	[mpm]	1.0	4.0
Rotation speed of MG roll	V_g	[rpm]	64	64
Circumferential speed ratio			1.0	0.3, 0.6, 1.0, 1.2

2.2. Nanosheet film thickness measurement method

The width of the film board was 100 mm. The 5 mm on both ends were not used because the surface tension made both ends of the film uneven. Therefore, the nanosheets peeled off from the film were cut at 10 mm × 90 mm as shown in Figure. 3, and only the nanosheets were peeled off and closely attached to a silicon substrate. The nine points were measured at 10 mm intervals. A surface shape measuring instrument (Dektak, BRUKER) was used to measure the thickness of the nanosheets. At the time of measurement, a groove was made with tweezers in the cross-machine direction (CD), and the difference in unevenness was taken as the film thickness.

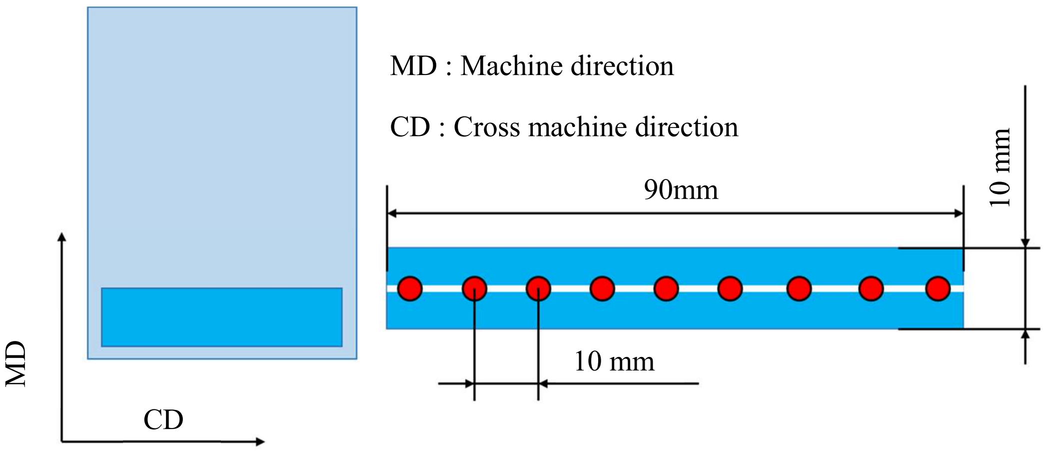


Figure 3. Overview of film thickness measurement; The dimensions of the test pieces are that the width of the films is 100 mm, and the thickness of the nanosheets is thinned at the edges due to the effect of surface tension. Therefore, the edges were cut off by 10 mm for measurement.

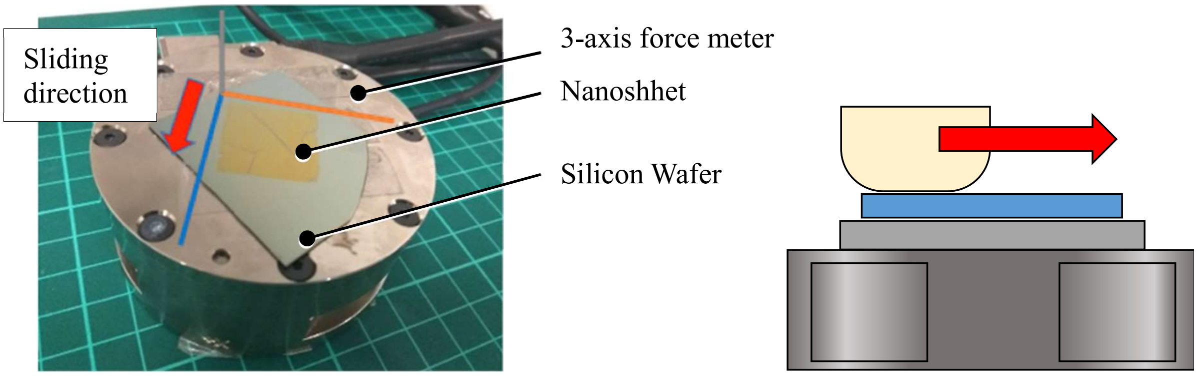
2.3. Method for measuring sliding frictional force between nanosheets and fingertips

A 3-axis force meter (ATI F / T Sensor Gamma, ATI Industrial Automation) in Figure 4 was used to measure the frictional force between the nanosheet and the skin. A silicon substrate on which a 20 mm × 20 mm nanosheet was placed, was fixed to a 3-axis force meter using double-sided tape. For friction measurement, a sliding experiment was conducted in the film transport direction, and the pad of the finger was pressed against the nanosheet and slid [9][10][11]. The sliding distance was set to 20 mm to keep the sliding speed as constant as possible during friction measurement, and sliding was performed for 5 s to obtain stable measured values. In addition, before the measurement, the test finger was washed clean with soap to remove sweat and oil generated on the skin, and the water on the finger surface was removed using an air spray. The change parameters in this experiment were the vertical load and the film thickness of the nanosheet, and the dynamic friction coefficients were measured at 0.4, 0.8, 1.0, and 2.0 N for the vertical load and 50, 100, 150, and 200 nm for the film thickness. Figure 5 (a)(b) shows the measured values. From Figure 5 (a), the area surrounded by the red frame was treated as the measured value, and the values at the beginning and end of applying the vertical load such as the blue frame and the green frame were excluded from the measured values. The combined force of F_x and F_y obtained by the measurement was defined as the frictional force F_t. The combined frictional force Ft

was calculated by substituting the frictional force (sliding direction) F_x and F_y into Eq. (1). In addition, the friction coefficient was calculated by substituting the friction forces F_t and F_z into Eq. (2).

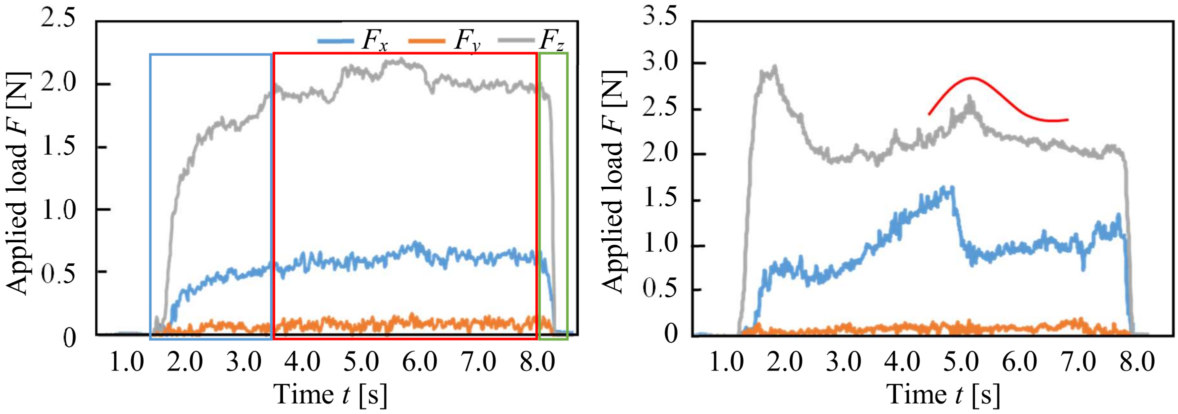
$$Ft = \sqrt{F_x^2 + F_y^2} \tag{1}$$

$$\mu = F_t / F_z \tag{2}$$



(a) (b)

Figure 4. Friction measurement in vivo and Friction method; (a) This friction measuring instrument can measure loads on three axes., (b) The measuring instrument and the silicon substrate were attached with double-sided tape so that the silicon substrate would not shift when sliding.



(a) (b)

Figure 5. Friction force measurement (a)Main data; (b) Not included as data

At this time, the measurement results in which stick-slip occurred was excluded from the calculation as shown in Figure 5 (b).

2.4. Method of measuring the contact area between nanosheets and fingertips

Figure 6 shows the visualization way of the contact area between the nanosheets and the fingertips. A jig for fixing the prism was mounted on the 3-axis force meter, and a 100 nm nanosheet was attached on the prism to visualize the contact area between the fingertip and the nanosheet under each load at a constant sliding speed. The contact face was taken with a CCD camera (60x) by irradiating the light source incident on the prism. At this time, the contact area part was the dark part, and the non-contact area part was the bright part. To calculate the contact area ratio from the obtained image, binarization was performed using the Vision Assistant, and the contact area rate was calculated by dividing the number of pixels in the dark area by the number of pixels in the image.

3. Results and discussion

3.1. Nanosheet film thickness measurement results and discussion

Figure 7 (a) and 7(b) show the results of nanosheet film thickness measurement. From the film thickness measurement results, nanosheets with a uniform film thickness could be produced at a solution concentration of 10 mg/ml and 20 mg/ml with a circumferential speed ratio of 0.3 and 0.6. However, the circumferential speed 1.2 shown in Figure 7 (b) had a large error bar. This was due to the surface tension of the bead formed between the film and the MG roll became unstable when there was an increase in solution concentration and the circumferential speed ratio of 1.0 or more, and the bead could

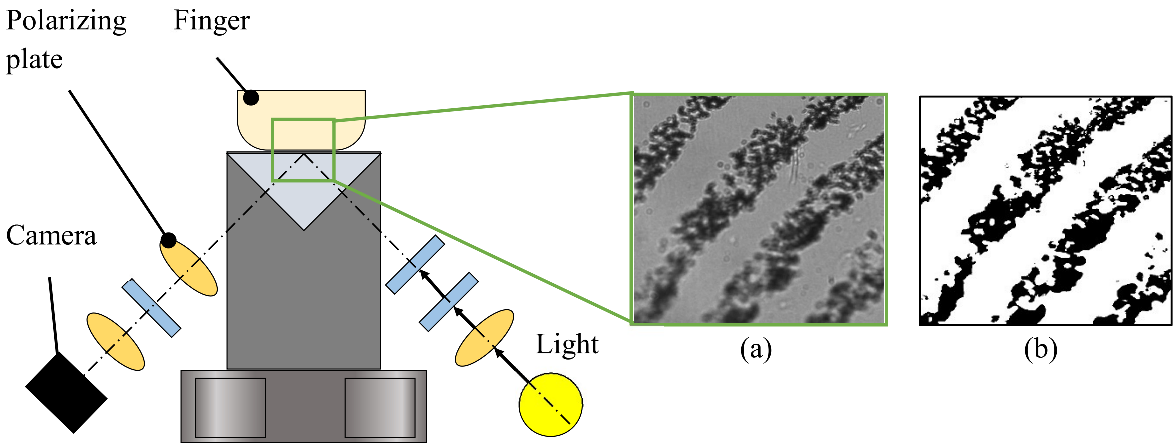


Figure 6. Outline diagram of contact surface visualization method; (a) The true contact surface of the fingerprint taken. (b) The truth contact surface has been binarized.

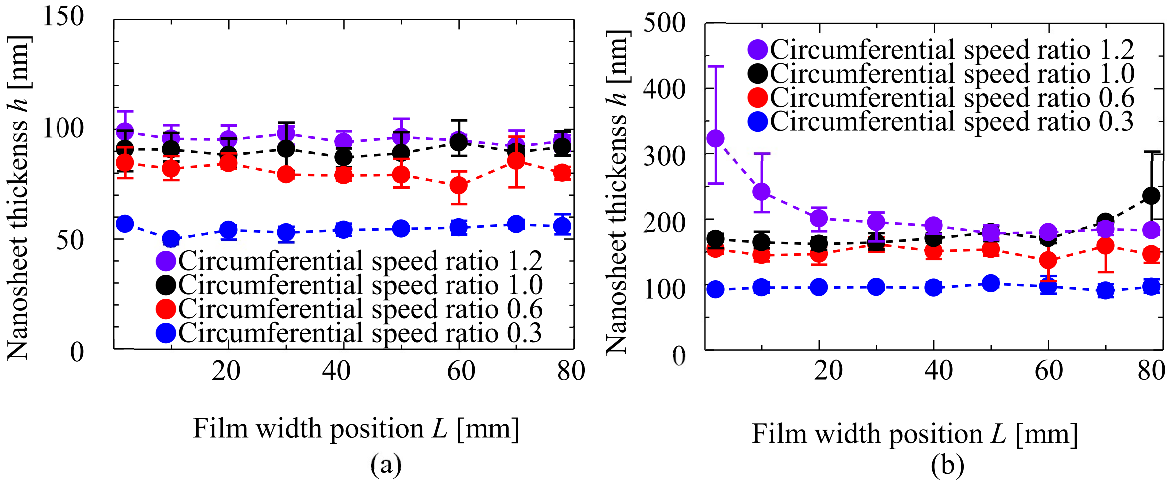


Figure 7. Nanosheet thickness measurement result (a) Solution concentration is 10mg/ml; (b)Solution concentration is 20mg/ml.

not be maintained stably. Therefore, in order to maintain surface tension, it was necessary to consider a circumferential speed ratio suitable for the solution concentration.

3.2. Sliding friction force measurement results and consideration

Figure 8 shows the friction coefficient and contact area ratio at each load between the nanosheets and the human skin fingerprint. The red plots show the means of the 10 experiments, and the error bars show the standard deviations. The triangular plot is the truth contact area ratio. Figure 8 shows the coefficient of friction decreases as the vertical load increases. However, when $F_z = 2.0$N, the coefficient of friction increased. In addition, the contact area increased as the vertical load increased. Similar results have been obtained from past studies in the dry state [5][6]. Also, the friction coefficient was high even though the contact area ratio was low at $F_z = 0.4$N. The adhesion mechanism between the fingerprint surface and the nanosheet, when the friction coefficient increases even though the contact area ratio is small at Fz = 0.4N, is thought to be that the finger with a small load is less likely to secrete sebum than the finger with a large load, resulting in a greater force for the nanosheet to stick to the finger surface. This is because the finger with a small load is less likely to secrete sebum than the finger with a large load. It is probable that the fingertips and the nanosheets were in a mixed lubrication state near $F_z = 0.4$ to 1.0 N. In addition, the coefficient of friction between the nanosheet and the fingertips was slightly increased compared to $F_z = 2.0$ N, as the vertical load increased, the fingertips became hot, and the body tried to maintain body temperature [11][12][13]. It is considered sebum that functions as a cooling agent is generated, and as shown in Figure 9, sebum acts as a lubricant when it enters the recesses of the fingerprint, and the coefficient of friction is slightly increased. Also, the surface structures of the nanosheet before and after sliding were observed using a desktop scanning electron microscope (NeoScopeTM, JCM-6000Plus, JEOL).

Figure 10 shows the observation image. Figure 10 (a) is before sliding, and Figure 10 (b) is after sliding. From Figure 10 (b), wear marks containing oil can be observed along the sliding direction. However, no wear marks such as shavings from fingers were found on the surface of the nanosheet shown in Figure 10 (b). Therefore, it is thought that this wear mark is due to oil. This oil is thought to contain sebum and sweat. Figure 11 shows the coefficient of friction at each film thickness when the vertical load is $F_z = 1.0$ N. The horizontal axis shows the thickness of the nanosheet, and the vertical axis shows the coefficient of friction. The round plot shows the first sliding of each film thickness, and the square plot shows the coefficient of friction due to the sliding after the first sliding. From Figure 11, it was found that the coefficient of friction also increased as the film thickness of the nanosheet

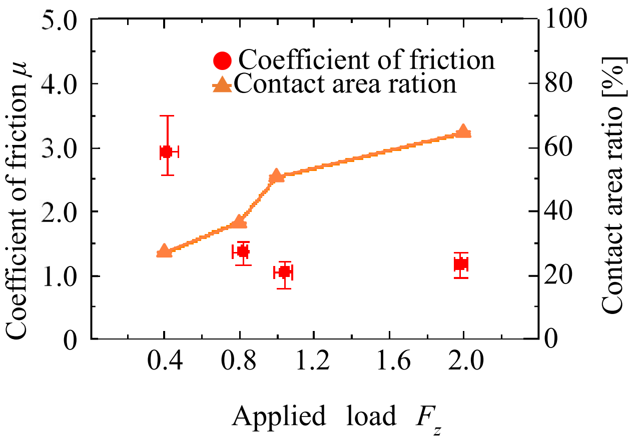


Figure 8. Coefficient of friction under applied load

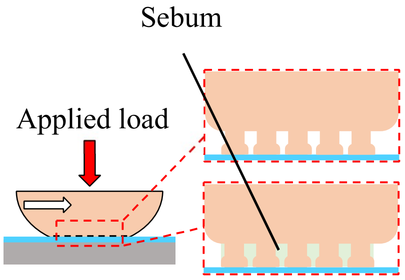


Figure 9. Consideration of contact between nanosheet and finger part.; By sliding, the temperature of the skin surface rises and sebum is released.

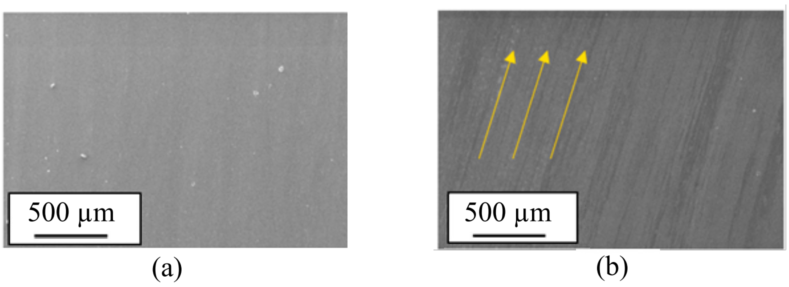


Figure 10. Nanosheet surface before and after the experiment; (a) Nanosheet surface before sliding; (b) Nanosheet surface after sliding.

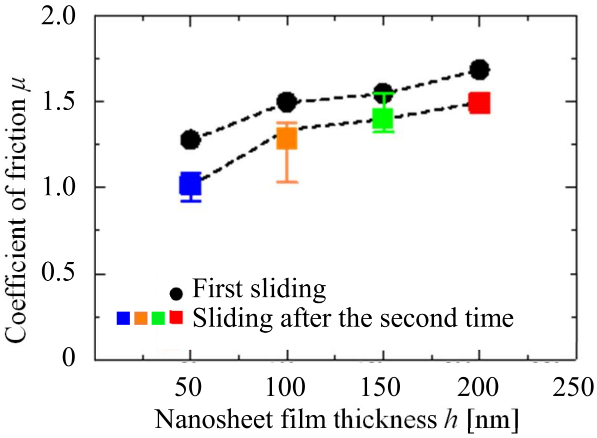


Figure 11. Coefficient of friction in thickenss of nanosheet

increased. The increase in the coefficient of friction is thought to be due to the increase in the contact area between the nanosheet and the fingertips due to the non-uniform film thickness after 100 nm. The coefficient of friction was lower after the second slide than after the first slide. There are two possible reasons for the difference in the coefficient of friction between the first sliding and the second sliding: first, the surface was slightly scraped by wear marks caused by sliding the nanosheet with the finger, and the true contact area with the fingerprint changed, which might be the reason for the lower coefficient of friction. The second reason could be that sebum secretion from the finger surface left residual sebum on the nanosheet surface after the first sliding.

4. Conclusion

In this study, nanosheets were produced by the micro gravure printing method, and the contact mechanism was investigated from the viewpoint of friction coefficient with the aim of clarifying the tribological characteristics between the nanosheets and human skin. The findings obtained from this study are shown below.

I. At a solution concentration of 10 mg/ml and a solution concentration of 20 mg/ml with circumferential speed ratios of 0.3 and 0.6, uniform nanosheets could be produced using a thin film coating machine using the R2R MG method.
II. It was confirmed that the coefficient of friction decreased as the vertical load increased except for the vertical load higher than $F_z = 2.0$ N.
III. It was confirmed that the coefficient of friction increased slightly when $F_z = 1.0$ N was exceeded.
IV. It was confirmed that the friction coefficient decreased as the contact area increased.

V. The sebum contained in the wear marks affected the friction between the nanosheet and human skin.
VI. A different coefficient of friction was observed between the first sliding and the subsequent sliding.

Conflict of interest

The authors have no competing interests to declare that are relevant to the content of this article.

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