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Microstructure Fabrication on Poly (L-lactic acid) Nanosheets Using Micro Gravure Printing Method

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Abstract

In this study, we examined the fabrication of polymer ultra-thin films (nanosheets) using a micro gravure printing method. Conveying speed of the plastic film substrate, the concentration of solution, rotating speed of the micro gravure roll ware investigated experimentally for effects on the film thickness of the nanosheets. And, we evaluated the Young's modulus of the nanosheets were fabricated, also investigated in detail the physical properties such as flexibility and surface roughness, in addition, surface of the nanosheet was microfabricated by embossing. Thereafter, the surface was observed using a laser microscope. It was possible to obtain new knowledge about the creation process nanosheets using the micro gravure printing method and embossing.

KeyWords: Nanosheets, PLLA, Micro gravure printing, Embossing, Roll to roll

1 Introduction

In recent years, fabrication of nanosheets with a typical thickness of 100 nm or less attracts great attention of many researchers. Nanosheets as an ultrathin nanostructure have some advantage e.g., high adhesion, high adhesion, high flexibility, high transparency, etc. In general, nanosheets are fabricated by spin coating method, however, it is difficult in mass-production by using spin coating. To solve this problem, a manufacturing method combine a micro gravure printing (MG) method with roll-to-roll (R2R) fabrication process is proposed. R2R is a production system using a complex fabrication procedure of rolling, stretching, coating, heat-treating, etc., is carried out continuously and finally wound in a roll form. And as one-step printing system, incorporating the MG method into the printing process makes it possible to fabricate nanosheets in mass production. The advantage of the MG method is that problems such as uneven coating and wavy pattern are eliminated over conventional gravure printing, and stable coating is enabled. However, since mass production of nanosheets has never been done so far, establishment of thin film control technology has not been done. The purpose of this study is to investigate the influence that transportation speed of film, rotational speed of micro gravure roller and concentration of solution have on the film thickness and evaluate the mechanical properties of nanosheets. e.g., Young's modulus and surface roughness. In addition, we fabricated honeycomb nanosheet using embossing [8].

2 Experimental apparatus and method

2.1 Fabrication of nanosheets using micro gravure printing

Table 1 shows the parameters for solutions used in the experiment. First, the polyethlene terephthalate (PET) film (thickness 100 μm, width 100 mm) as substrate was placed through roller. After that, the tension load was applied to the film. And then, polyvinyl alcohol (PVA) was coated on the PET film substrate as to release the nanosheets from the PET film substrate by sacrificial layer method as shown in **Fig. 1**. Finally, polylactic acid (PLLA) was coated, and the

Table 1 Type of solutions

	Sacrificial layer	Nanosheet
Solute	Poly (vinyl alcohol) (PVA)	Poly lactic acid (PLLA)
Solvent	Water	Chloroform

coated film was immersed in water. The sacrificial film was dissolved and removed in water, therefore, the nanosheets was able to be peeled off. In this study, thickness of nanosheet was measured using a stylus type surface profile, the effects of transportation speed of film, rotational speed of micro gravure roller, concentration of solution on film thickness are tested by each parameter. Furthermore, the Young's modulus of nanosheets was measured by using SEIBIMM method [8].

2.2 Measurement of Young's modulus by nanosheets using SEIBIMM method

The Young's modulus in the machine direction and cross machine direction at each film thickness of the produced nanosheets was measured by SEIBIMM method. The SEIBIMM method is a test that can easily measure the Young's modulus of a thin film. A nanosheets was attached to PDMS (silicone rubber) of 4.0 cm^2. Using the Young's modulus measuring instrument shown in **Fig. 2**, the PDMS was stretched 2.0 mm (~10 % strain), the wrinkles of the resulting nanosheets were observed with a laser micro scope, the length between the measured wrinkles and wrinkles was substituted into the following equation, Young's modulus is calculated. Also, the appearance of the wrinkles observed is shown in **Fig. 3**.

$$E_{PLLA} = \frac{3E_{PDMS}}{\left(1-\upsilon_{PDMS}^2\right)}\left(\frac{d}{2\pi h}\right)^3\left(1-\upsilon_{PLLA}^2\right) \qquad (1)$$

Here, E is the Young's modulus, v is the Poisson's ratio, h is the film thickness of the nanosheets, and d is the length between wrinkles and wrinkles.

2.3 Measurement of surface roughness of nanosheets

The surface roughness of the nanosheets fabricated by using the spin coating method and the nanosheets fabricated by micro gravure printing was measured using a scanning probe microscope. The area of the nanosheets to be measured was set to 3.0 μm^2. In addition, the film thickness of each nanosheets is 80 ± 10 nm.

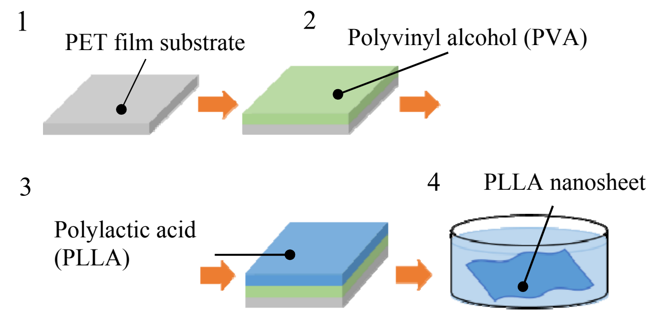


Fig. 1 Sacrificial layer method

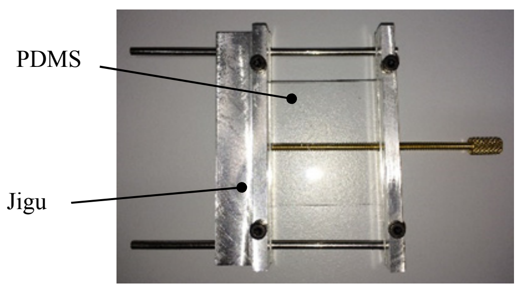
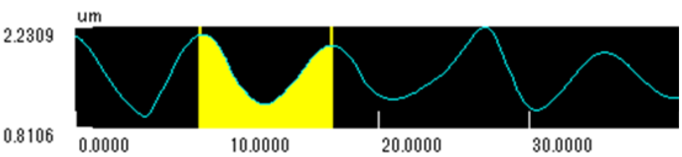
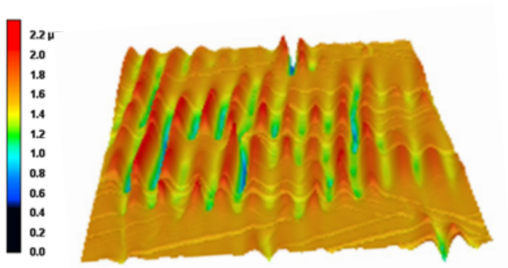


Fig. 2 Measuring instrument for Young's modulus



(a) Wrinkle and wrinkle distance on nanosheets



(b) Wrinkle and wrinkle distance on nanosheets

Fig. 3 Wrinkle on the nanosheets

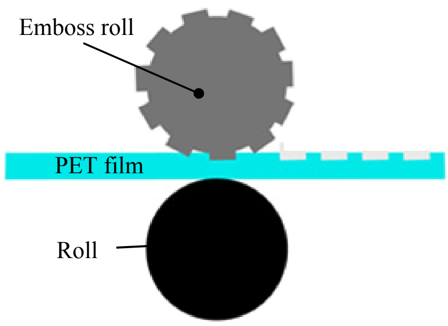


Fig. 4 Emboss processing

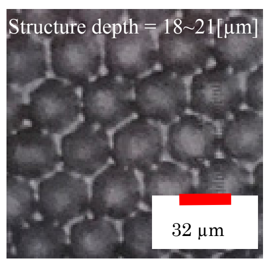


Fig. 5 The surface of the embossing roll

2.4 Fabrication of honeycomb nanosheets using mmbossing process and spin-coat method

Figure 4 shows schematic diagram of embossing process. **Figure 5** shows the surface of the honeycomb roll used in this experiment (pitch 32 µm, depth 18~21 µm, line width 1~2 µm, one side of a hexagon 17~18 µm). The embossing process was performed by using emboss machine to transfer honeycomb texture on the embossed roll to PET film substrate. First of all, emboss roll was heated to 150 °C and, PET film substrate was sandwiched between emboss roll and rubber roll. After that, a pressure of 200 kg/cm was applied to the upper embossing roll and the PET film was extruded at a speed of 2.0 m/min. nanosheets was fabricated using the prepared honey comb PET film substrate by spin-coating method. Nanosheets was observed by using a laser microscope as to confirm whether the honeycomb structure was transferred.

3 Experimental results and discussion

Figure 6 shows the relationship between thickness and the transportation speed of film under solution concentration of PLLA *c*=10 mg/mL. Each plot shows the average of five experiments, and the error bars show the variation. From the experimental results, the film thickness was decreased with increase in transportation speed of film. Because, of the supply delay of the coating liquid from the micro gravure roll. Moreover, it is understood that variations of the faster transport speed are low. It seemed that a strong force of liquid pool is formed between the film and the micro gravure roll, and this particular force is pulled from both the film and the micro gravure roll (smooth effect). In this experiment, focusing on producing a nanosheet with a film thickness of 60 nm, from this graph, as to reduce uneven coating, the rotation speed of the micro gravure roll.

Figure 7 shows relationship between thickness and the peripheral speed ratio. Each plot shows the average of triplicate experiments, and the error bars show the variation. From the Based on the experimental results, the film thickness was increased with increase in peripheral speed ratio. Also, the unevenness of coating was decreased. As the result, there is a change in the amount of pooled liquid between the two surfaces. When the peripheral speed ratio is 0.3, and 0.6, the rotation speed of the micro gravure roll is slower with respect to the conveying speed of the film, the supply of the solution to the liquid pool by the micro gravure roll is inadequate, and the liquid pool becomes unstable. Therefore, unevenness of coating is likely to occur. On the other hand, when the peripheral velocity ratio is 1.0, it is considered that the supply of the solution by the micro gravure roll is sufficient and the liquid pool is pulled with the same force from both the film and the micro gravure roll, so that unevenness is unlikely to occur. Therefore, by setting the peripheral speed ratio to 1.0, the occurrence of unevenness can be suppressed.

Figure 8 shows relationship between thickness and the concentration of solution. Each plot shows the average of triplicate experiments, and the error bars

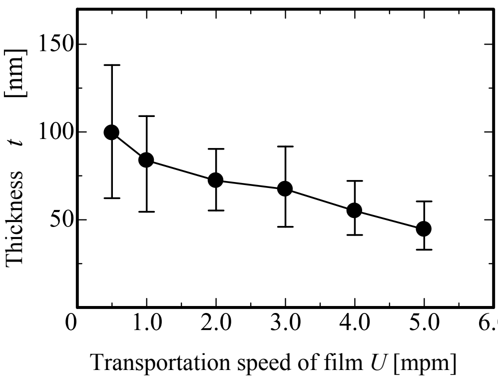


Fig. 6 Thickness of the nanosheets while changing transportation of film

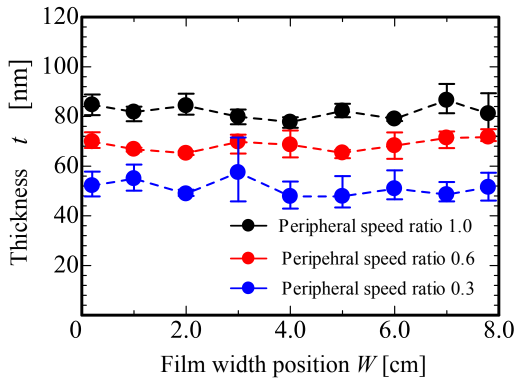


Fig. 7 Thickness of the nanosheets while changing peripherao speed ratio

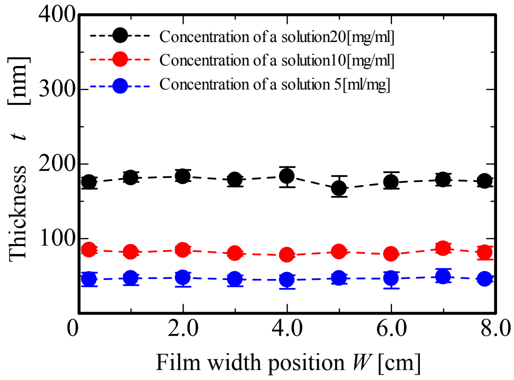


Fig. 8 Thickness of the nanosheets while changing peripherao speed ratio

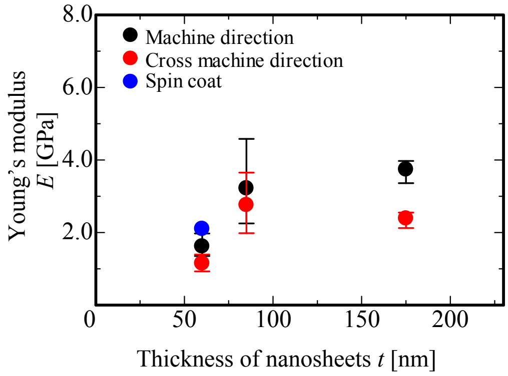
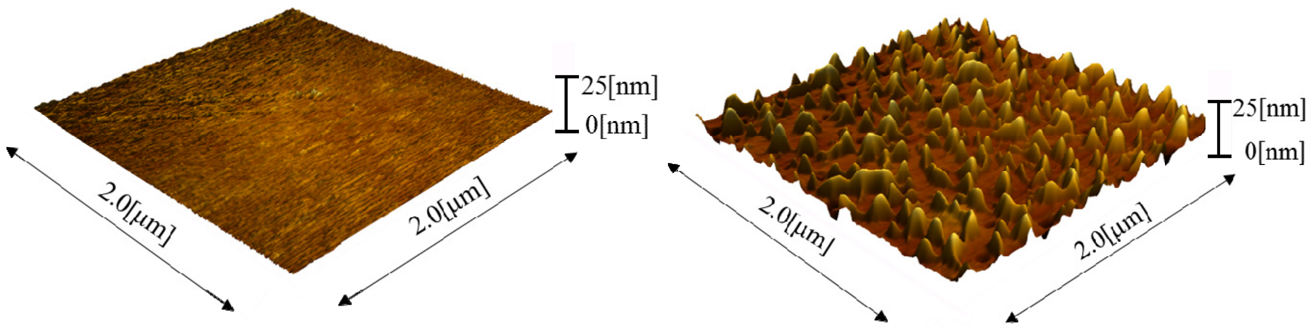


Fig. 9 Young's modulus in each film thickness

show the variation. Based on the experimental results, the film thickness was increased with increment on the concentration of solution. However, unevenness of coating was increased. As the result, it is conceivable that the viscosity increased with increasing concentration. Since the scooped solution is controlled by the doctor blade of the micro gravure roll which removes excess solution. The amount of liquid is constantly pooled between the two surfaces, but as the viscosity increases the amount of solution coated on the film increases. Therefore, as the concentration of the solution to be coated is increases, the liquid breakdown is more severe with higher chance of the occurrence of is an influential factor on the occurrence of coating unevenness.

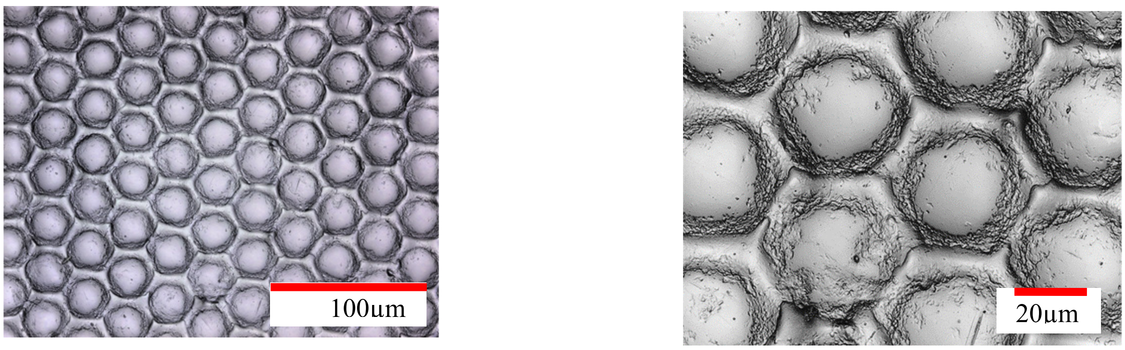
Figure 9 show the Young's modulus of nanosheets in each film thickness. Based on the experimental results, the fabricated nanosheets in this experiment showed anisotropic property in the elastic modulus in the machine direction and the cross machine direction. Since nanosheets is applied to the machine direction, it is considered that shearing stress was applied during coating and anisotropy occurred. Roughness of the nanosheet fabricated by micro gravure printing was 2.97 nm. From the figure, it is understood that the surface roughness of the nanosheet produced by micro gravure printing is larger. It is conceivable that aggregation occurs when the film is coated on the film from the liquid reservoir and when the film is taken up.

Figure 10 shows the surface roughness of nanosheets different in fabrication method. The surface roughness of the nanosheet fabricated by the spin



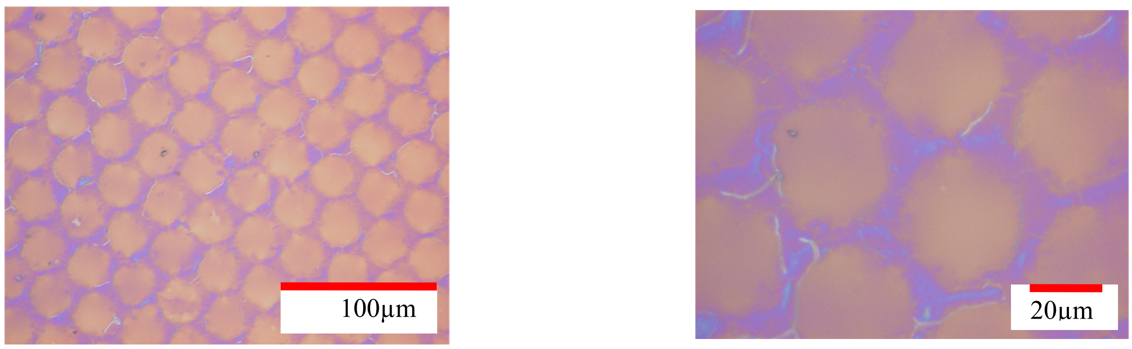
(a) Nanosheets fabricated by spin coating **(b) Nanosheets fabricated by micro gravure printing**

Fig. 10 Surface roughness of nanosheets



(a) 50 magnification **(b) 150 magnification**

Fig. 11 Laser microscope images of honeycomb PET film



(a) 50 magnification **(b) 150 magnification**

Fig. 12 Laser microscope images of honeycomb nanosheets

coating method was 0.62 nm, and the surface roughness of the nanosheet fabricated by micro gravure printing was 2.97 nm. From the figure, it is understood that the surface roughness of the nanosheet fabricated by micro gravure printing is larger. It is conceivable that aggregation occurs when the film is coated on the film from the liquid reservoir and when the film is taken up.

Figure 11 shows an image of a honeycomb PET film taken with a laser microscope. This honeycomb PET film was fabricated under the following experimental conditions (temperature:150 °C, speed:2 m/min, pressure: 200 kg/cm). It was found that the surface Embossing roll was successfully transferred. Finally, the nanosheets were fabricated based on this textured film.

Figure 12 shows an image of a honeycomb nanosheets taken with a laser microscope. The thickness of nanosheets could be controlled by the rotation speed of the spin-coat. The surface texture of the honeycomb film was sufficiently transferred. However, some transferred patterns on the nanosheets are slightly torn and connected to adjacent micro-structures (Fig 8 (b)). In the honeycomb PET film.

4 Conclusion

In this study, the influence of film conveying speed, peripheral speed ratio, solution of concentration on film thickness of nanosheet was experimentally investigated, in addition, a honeycomb structure nanosheets was fabricated by embossing process. Consequently, following knowledge were obtained.

(1) The film thickness of the nanosheets became thinner as the film conveying speed increased.
(2) By setting the peripheral speed ratio to 1.0, the film thickness of the nanosheets became thick and unevenness could be decreased.
(3) By decreasing the concentration of the solution, the film thickness of the nanosheets became thicker and unevenness could be decreased.
(4) The Young's modulus of the nanosheets became smaller as the thickness of the nanosheets thinner. Also, the anisotropy of the nanosheets due to unevenness was considered.
(5) We succeeded to transfer the microstructure of the PET film directly to the nanosheets.
(6) A nanosheet having a honeycomb structure could be prepared.

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