

Properties of Self-Assembled Monolayer as an Anti-adhesion Layer on Metallic Nano Stamper

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ABSTRACT

In the nano replication process, surface quality can be determined by the interfacial phenomena such as the wettability and adhesion force between the metallic stamper and replicated polymeric patterns due to high ratio of surface areas to volume. An experimental method is presented to analyze the temperature dependency on the anti-adhesion property between the stamper and polymer. To analyze the wettability between the stamper and polymer, contact angle of pliable polymer on the metallic stamper was measured at actual molding temperature. To reduce sticking between the stamper and replicated polymeric patterns, SAM (self-assembled monolayer) was applied to the nano replication process as an anti-adhesion layer. Alkanethiol SAM was deposited on nickel surface using solution deposition method. To examine the effectiveness of the SAM deposition on the metallic stamper, contact angle and LFM (Lateral Force Microscopy) were measured.

Keywords: wettability, self-assembled monolayer, anti-adhesion layer, metallic stamper, releasing process

1 INTRODUCTION

With the increasing demand for micro/nano polymeric components, nano-molding using the nano stamper has received much attention. But many technical problems in this molding process have to be overcome for the mass-production of components at low cost. For example, as the features of the nano patterns on the stamper become smaller, surface quality and transcribability are governed by the interfacial phenomena such as the wettability and adhesion force between the stamper and replicated polymeric patterns, due to high ratio of surface areas to volume [1]. High molding temperature and several surface modifications can solve these interfacial problems. Therefore, it is necessary to analyze quantitatively the effects of the mold temperature on the anti-adhesion property between the stamper and polymer in a pliable state especially at temperatures above the glass transition temperature of the polymer. These interfacial problems can also be solved by several surface modifications using an anti-adhesion layer. SAM (self-assembled monolayer) is a candidate material for the anti-adhesion layers deposited on the nano patterns. SAM is stable physicochemically and can

control surface properties of the stamper surface [2,3]. Although nickel substrate is a superb material for the nano stamper, it is not an easy process to deposit SAM on the nickel stamper due to the difficult pretreatment to reduce oxide layer on nickel [4].

To analyze the anti-adhesion property of the stamper precisely, a polymer in a pliable state was used at temperatures above the glass transition temperature. Only a few researchers have measured the contact angle using the polymer in a pliable state, because the high viscosity and the thermal instability of the polymer in a pliable state have made experiments difficult. Grundke et al. [5] and Wulf et al. [6] analyzed the wetting tension and the surface tension of polymer melts as a function of temperature below the melting temperature. However, the anti-adhesion property between the actual stamper and the polymer has not been analyzed. In the analysis of the anti-adhesion property between the stamper and the polymer, the contact angle should be evaluated at the actual molding temperature.

In this study, SAM was applied as an anti-adhesion layer to replication process to reduce the interfacial phenomena between the nickel stamper and replicated polymeric patterns. The effectiveness of SAM deposited on nickel stamper was verified through measuring contact angle and lateral friction force. And to analyze the effectiveness of SAM on surface quality of replica in actual nano releasing process, the correlation between the nickel stamper and polymer in actual molding temperature was analyzed as the precedence experiments. To analyze the stability of SAM in actual molding temperature, anti-adhesion properties of SAM were measured for different maximum molding temperature.

2 EXPERIMENTAL PROCEDURES

2.1 Contact angle measurement between the stamper and the polymer at actual molding temperature

Figure 1 shows the schematic diagram of the contact angle measurement system. This system consists of the hot plate and the thermal chamber, which are used to heat the air in the thermal chamber up to the temperature of the actual molding process. The hot plate was connected to the temperature controller and temperature of the stamper surface in the thermal chamber was measured with a thermometer. PC (Polycarbonate) and PMMA (Polymethyl

Methacrylate) were used as the polymer material, and they were used in the measurement of the contact angle on the stamper. The contact angle was measured by using the polymer in a pliable state at a temperature above the glass transition temperature, T_g , of the polymer. The temperature of the hot plate in the contact angle measurement system was maintained at 180°C for about 30 minute. And then, at this temperature the thermal chamber was further heated to the peak mold temperature and maintained at the peak mold temperature for 15 minutes. After the stamper was cooled, the contact angle was measured.

2.2 SAM deposition method and analysis of anti-adhesion properties

The nickel stamper was pretreated by an electrochemical reduction method to remove oxide on the nickel stamper surface. And then using the solution deposition method, alkanethiol SAM as an anti-adhesion layer was deposited on nickel as shown in Figure 2 [4].

To examine the effectiveness of the SAM deposition on the metallic stamper, we analyzed the change in the surface property of SAM deposited nickel stamper. First, to compare the changes in the surface properties between the bare nickel stamper and SAM-deposited nickel stamper, contact angles were measured at room temperature, and the lateral friction force was measured.

However, actual replication processes are performed under various process conditions and environments. To analyze the change in the surface energy of a SAM deposited nickel stamper at these conditions, the contact angle and lateral friction force were measured at the actual processing temperature for the case of compression

molding and injection molding. Considering conventional molding condition, temperatures were selected from 100°C to 300°C. In this range, SAM on the nickel substrate was heated for 5 minutes at different maximum molding temperatures. Then, it was cooled at room temperature, and the contact angle and lateral friction force were measured.

3 RESULT

3.1 Wettability between the stamper and a polymer in a pliable state

Figure 3 shows the dependence of the terminal contact angle at peak mold temperatures of the PMMA and the polycarbonate. As shown in Figure 3, as the peak mold temperature increases, the terminal contact angle values decreases for each polymer material. When peak mold temperatures of PMMA were changed from 210 to 220 °C, the contact angle values decreased markedly. This temperature range includes the melting temperature, T_m , of the PMMA. This behavior indicates that when the fluidity of PMMA at T_m increased, the wettability between the stamper and the PMMA increased.

To evaluate contact angle of the stamper and measure the surface quality and replication quality of the molded substrates at various molding temperatures, we fabricated polymeric replication using the nickel stamper. Molding temperatures were the same as the peak mold temperature in the contact angle measurement in the range of 180 °C to 250 °C. Compression molding with powdered PMMA and PC was used to fabricate a plastic substrates.

Surface roughness of the molded substrate was measured by AFM (Atomic Force Microscopy). Figure 4 shows the effect of mold temperature on the surface roughness of the molded substrate and the contact angle of the stamper. As shown in Figure 4, as the mold temperature increased, the surface roughness of the molded substrates increased while the contact angle value of the stamper decreased. The surface roughness tended to be inversely related to the contact angle value. This result shows that an increase in the wettability of the stamper surface deteriorates anti-

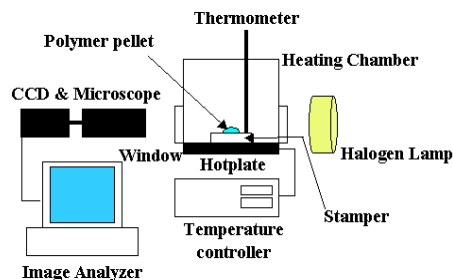


Figure 1: The experimental setup for contact angle measurements

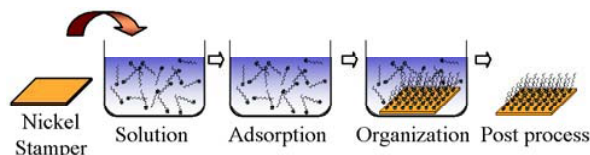


Figure 2: SAM deposition on nickel stamper using solution deposition method

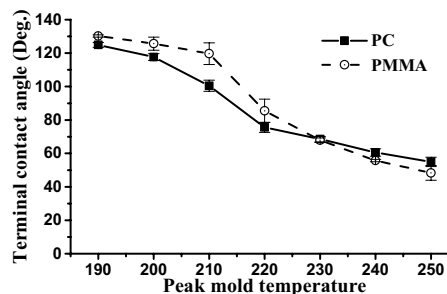
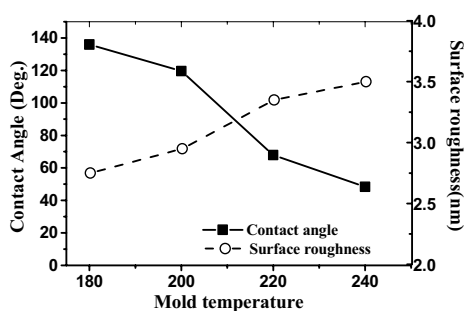
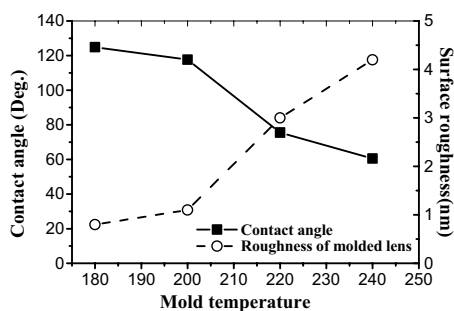


Figure 3: The terminal contact angle by the PMMA and the PC for various peak mold temperature



(a) PMMA



(b) PC

Figure 4: Comparison between surface roughness of the molded plastic substrate and contact angle of the stamper at various mold temperature

adhesion properties between the stamper and the polymer. This deterioration of anti-adhesion properties between two surfaces again results in the deterioration of the surface quality of the molded substrates.

3.2 The comparison of the bare nickel stamper and the SAM-deposited nickel stamper

To increase the surface quality of replicated polymeric substrates, SAM was applied to nickel stamper as the anti-adhesion layer. To verify effectiveness of the SAM-deposited nickel stamper, the contact angle and lateral friction force of both the bare nickel stamper and the SAM on the nickel stamper were measured at room temperature. As shown in Figure 5, the contact angle between nickel stampers and D.I water increased from 70.37° to 109.22° after SAM deposition. The comparison of surface properties between the bare nickel stamper and the SAM deposited nickel stamper was summarized in Table 1. The wet energy datas of surfaces were calculated from the contact angle and the surface energy of SAM deposited nickel stamper decreased markedly. Figure 6 shows the lateral friction forces for different normal forces and it is vafied that the higher normal force was, the lower lateral friction force was measured in SAM deposted nickel

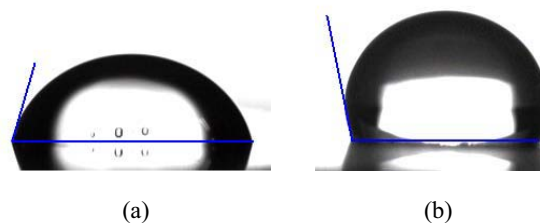


Figure 5: Contact angle of (a) the bare nickel stamper and (b) the SAM deposited nickel stamper at room temperature

	Bare nickel stamper	SAM deposited nickel stamper
Contact angle (°)	70.37	109.22
Wet energy (mN/m)	24.46	-23.97
Lateral friction force (eV)	0.0969	0.0605

Table 1 Comparison of surface properties between the bare nickel stamper and the SAM deposited nickel stamper for 10nN normal force of LFM

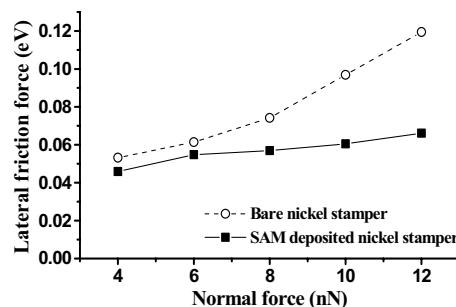


Figure 6: Lateral friction force for different normal forces for the bare nickel stamper and the SAM-deposited nickel stamper.

stamper. The comparison of surface properties between the bare nickel stamper and the SAM-deposited nickel stamper based on these measurement results indicates that surface energy can be reduced by SAM-deposition. Therefore, these results imply the feasibility of SAM being used as an anti-adhesion layer for improving the surface quality of the molded polymeric nano patterns in the nano replication process.

3.3 Change of SAM properties at actual molding conditions

Figure 7 shows the water contact angle and the lateral friction force of SAM-deposited on the nickel stamper for different maximum molding temperatures. The contact

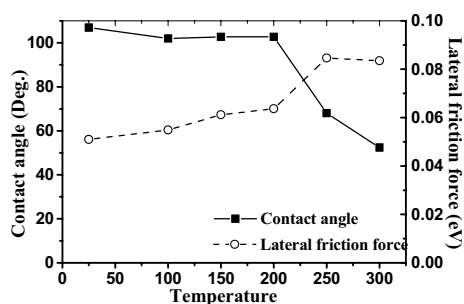


Figure 7: Water contact angle and lateral friction force as function of maximum molding temperature; SAM-deposited nickel stamper was cooled at room temperature after heating at different maximum molding temperatures for 5 minutes

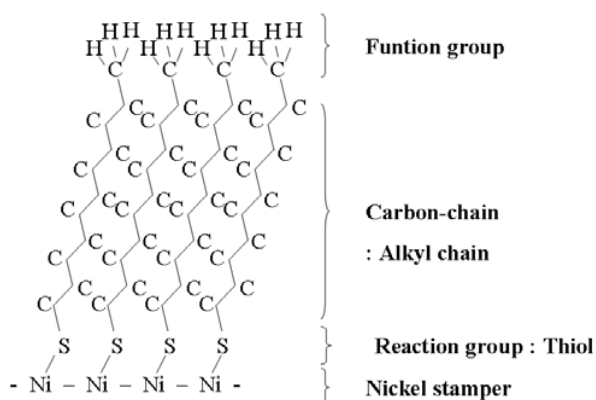


Figure 8: Structure of SAM binding nickel stamper

angle maintained up to the maximum molding temperature of 200°C and markedly decreased after 200°C, as shown in Figure 7. Also, Figure 7 shows that lateral friction force maintained up to 200°C similar to contact angle and markedly increased over 200°C.

These tendencies were caused by the damages in carbon-chain structures of SAM, as shown in Figure 8. Since the monolayer is composed by carbon-chains of alkanethiol bound by van der Waals force, the excessive heat energy can break down carbon-chain structure of SAM. The damages, due to heat energy, deteriorated the anti-adhesion properties of SAM and the effectiveness of SAM to metallic stamper may deteriorate. However, it is expected that SAM deposited stamper can be used in the replication process, because the molding temperatures of hot embossing and injection molding are lower than 200°C, the polymer resin in molding is generally filled and cooled in mold cavity for a few seconds.

4 CONCLUSION

We presented the feasibility of SAM as anti-adhesion layer to nickel stamper. To verify the effectiveness of SAM, it was analyzed that the surface energy of stamper influenced the surface quality of replica. The contact angle was measured at the temperature set for the actual nano-molding process, in which the stamper was heated above the glass transition temperatures of the PMMA and PC. Using these results, we verified that surface quality of replica fabricated using stamper deteriorated as the molding temperature increased. The anti-adhesive property of nickel stamper in replication could be improved by depositing SAM on the nickel stamper. The contact angle and the lateral friction force were measured and anti-adhesion properties of SAM were analyzed. And the stability of SAM in actual molding temperature was analyzed

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