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# Development of release agent-free replica mould material for ultraviolet nanoimprinting

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ABSTRACT

Ultraviolet nanoimprint lithography (UV-NIL) is very useful technique for the fabrication of nanopatterns. Replica mould materials that can be cured by UV radiation have been studied for the purposes of master mould reproduction and for wrapping around roll moulds. In our previous study, aimed at the production of high-aspect-ratio nanopatterns, we needed a harder replicating material. We have therefore developed a hard UV-curable resin with an antifouling effect. This material consists of a blend of a cationically polymerizable UV-curable resin and an epoxy-modified fluorinated resin. By using this material, replica moulds with pillar or hole patterns were fabricated by UV-NIL. We carried out repetitive UV-NIL with these replica moulds and we evaluated the mould surface and the transferred UV-cured patterns. The replica mould with antifouling effect was shown to be suitable for use in UV-NIL without a release agent. The lifetime of the pillar-pattern replica mould was shorter than that of the hole-pattern mould, and the rate of increase in the error rate of the pillar-pattern replica mould was faster than that of the hole-pattern mould, whereas the rates of deterioration of both replica mould surfaces as determined by contact-angle measurements were the almost same. Therefore, error-rate measurements permit more-precise quantification of the release properties of the moulds. The shape dependency of the lifetime and the error rate might result from shrinkage of the transferred UV-curable resin after curing.



## 1. Introduction

Nanoimprint lithography (NIL) is a very useful technique for the fabrication of nanoscale patterns [1]. In the case of ultraviolet-NIL (UV-NIL) [2], the presence of a release layer on mould surface is important to prevent adhesion of the UV-curable resin [3–7]. A material for replica moulds that does not require a release agent is therefore urgently needed for NIL and roll-to-roll NIL technologies. In particular, a film-based replica material capable of transferring a master mould pattern by UV-NIL would have many advantages, such as a simpler pattern-transfer process, an improved ability to wrap around a roll mould, and better disposability. Available materials for the replica mould include polytetrafluoroethylene [8], ethylene–tetrafluoroethylene copolymer [9], and polyurethane acrylate [10]. However, all these materials suffer from a lack of hardness of the cured resin, in that they have pencil hardness ratings in the range B to H, making them soft materials. Our recently study revealed that the hardness of the cured resin of the replica mould is an important factor in the transfer of high-aspect-ratio nanoscale patterns [11]. Materials with greater pencil hardness are therefore needed. In a previous study, we developed an antifouling-effect UV-curable resin for fabricating antireflection structures [12]. This material was also sufficiently hard (pencil hardness 4H) to withstand touch or contact, making it suitable for use in replica moulds.

The UV-cured material, which has sufficient hardness and an antifouling effect, is suitable for use in producing replica moulds for UV-NIL. In addition, we have improved our previous UV-curable resin material and have used it to produce a replica mould. In this study, the properties of our revised UV-curable resin were investigated with respect to its use in replica moulds. In addition, we introduce an error rate, determined by statistical analysis [13] of the transferred dots patterns, as a means of quantifying the deterioration of the replica mould. This approach to the error rate by means of statistical analysis is described for the first time. The obtained error rates were also compared with other group error ratio results [14].

## 2. Experimental apparatus and procedures

In this study, two silicon moulds, one with a pattern of holes and one with a pattern of pillars, each with a diameter of 230 nm

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and a pitch of 460 nm, were used as the master moulds. A first replicated mould was fabricated by means of parallel-plate UV-NIL using a UV-curable resin (PAK-01CL; Toyo Gosei Co. Ltd., Tokyo) on a polyester film substrate (Cosmoshine A4300; Toyobo Co. Ltd., Osaka). The UV-NIL pressure was 0.25 MPa, the time was 5 min, and the UV exposure dose was 120 mJ/cm$^2$. The resulting replica moulds were coated with a layer of chromium up to 30 nm thick by using a resistively heated vacuum evaporation system (VPC-260F; ULVAC KIKO Inc., Saito City). A release layer of OPTOOL DSX 0.1 wt% (Daikin Industries, Ltd., Osaka) was then applied. (OPTOOL DSX did not coat the mould well without the chromium layer.) This first replication process is necessary to give replica-transfer moulds that have an antifouling effect and the same feature patterns as the master silicon moulds. Although the replicated pattern in PAK-01 coated with chromium and OPTOOL DSX can be used as a replica mould, the process is time-consuming and PAK-01 is a soft material. After the first replica-transfer moulds with pillar or hole patterns, respectively, had been prepared, a second series of replica moulds with an antifouling effect were fabricated as shown in Fig. 1.

In our previous study, the UV-curable antifouling material showed a poor sensitivity. We therefore developed a new UV-curable resin with improved sensitivity, which we named PARQIT OEX-028-X433-3 (hereafter, X433-3; Autex Co., Ltd., Tokyo). X433-3 consists of a blend of a cationically polymerizable UV-curable resin and an epoxy-modified fluorinated resin. The base cationically polymerizable UV-curable resin is alicyclic epoxy resin. We blended several alicyclic epoxy resins. One of typical alicyclic epoxy resin is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate and this structure is shown in Fig. 2. The fluorinated component of X433-3 segregates at the surface of the cured resin after heat treatment, as shown in Fig. 2, thereby

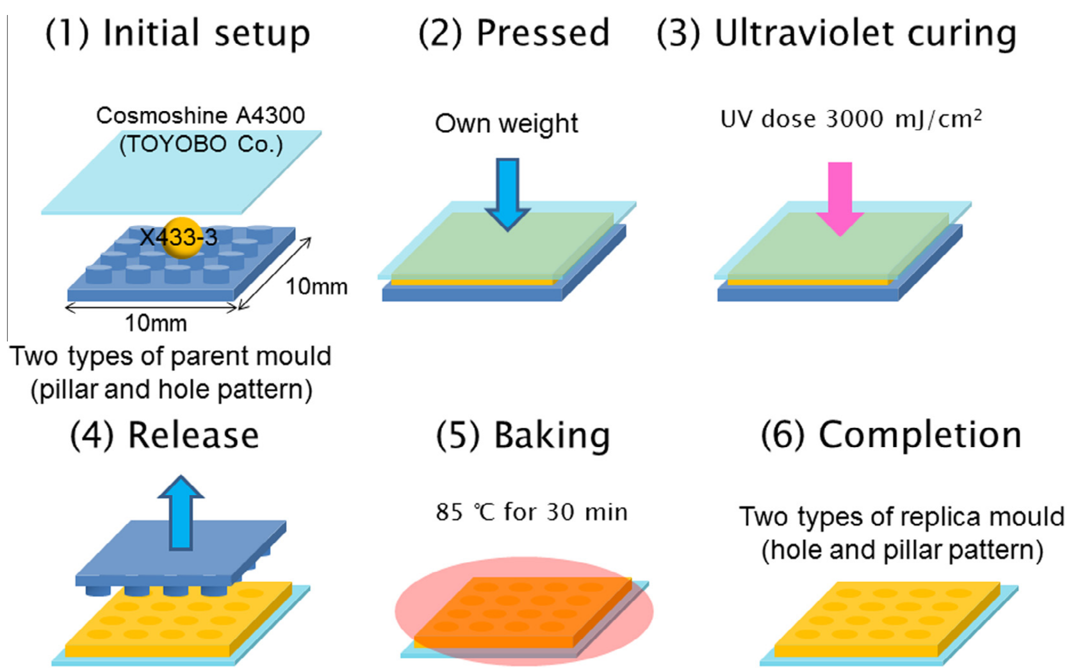


**Fig. 1.** Process for fabrication of the replica mould with an antifouling effect.

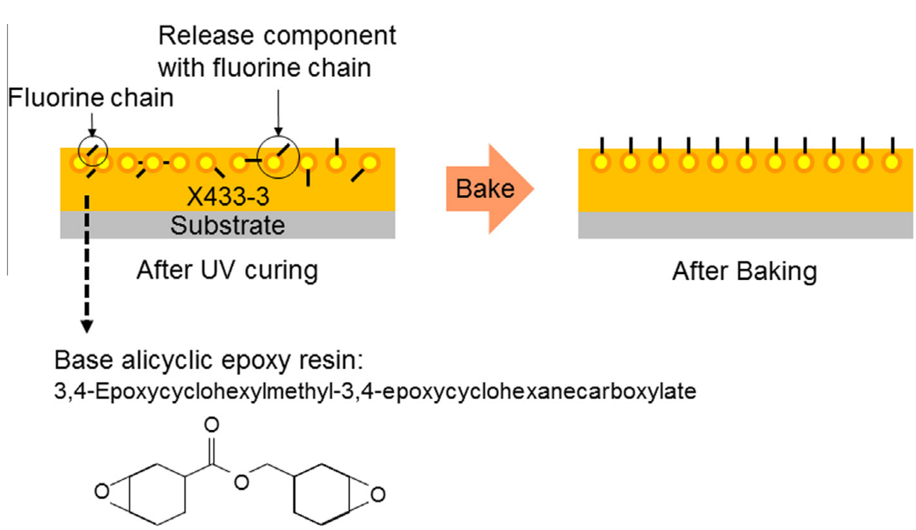


**Fig. 2.** Schematic illustrating the generation of an antifouling effect on the X433-3 surface by heating.