Dependence of demolding force on resist composition in ultraviolet nanoimprint lithography

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ABSTRACT

We investigated demolding force in UV nanoimprint lithography with different compositions of UV-curable polymer blends containing polypropylene glycol diacrylate as the base, trimethylolpropane triacrylate as the crosslinking agent and Irgacure 651 as the photo-initiator. The demolding force was measured using a tensile test machine with homemade fixtures. The variations of demolding force was compared to shrinkage due to the polymerization and Young’s moduli of cured polymer blends, determined by a simple optical method and atomic force microscopy, respectively. It was found that decreasing the content of the crosslinking agent from 49 to 0 wt% decreases the Young’s modulus from 30±3 to 12±3 MPa and that in turn decreases the demolding force by almost half, with no significant effect on pattern fidelity.

Keywords: Nanoimprint lithography, Demolding force, UV curing, chemical compositions.

1 INTRODUCTION

Nanoimprint lithography (NIL) initially introduced by Chou’s group [1,2] can be classified into two main categories; Thermal NIL [3,4] and ultraviolet (UV)-NIL [4,5]. Taking advantage of being a fast and room temperature process, low resist viscosity and therefore easy filling of resist into stamp cavities at the molding stage, UV-NIL strives to replace thermal NIL. However, most of UV resists are based on adhesive materials such as epoxy and acryl, and adhesion between the imprinted pattern and the mold surface could be significant, making it difficult to achieve high aspect ratio patterns and often resulting in structural failure during demolding.

Different schemes can be adopted to reduce the demolding force in thermal or UV-NIL. Taniguchi et al. [6] and Kim et al. [7] investigated the reduction in demolding force when anti-sticking agents such as silane molecules are either coated on the stamp or mixed with the resin. However, despite application of an anti-adhesion coating, the adhesion of the UV-resist to the stamp can be still significant. X. Ye et al. [8] investigated the effect of exposure time on demolding force in UV-NIL and found that partial curing of a UV resist lowers the demolding force. They suggested (although did not measure) that the decrease in demolding force is due to a lower Young’s modulus (E) of the resist when it is partially cured. However, it is difficult to use the partial curing of the resist as a process parameter because control and repeatability of the degree of curing are poor mainly due to the variation of UV intensity across a UV lamp, diffraction of UV light at the edges of mold insert and also exothermic and almost self-propelled nature of UV-polymerization reaction. Our group has recently reported systematic studies on the demolding process using a finite-element method (FEM) [9] as well as experimentally [10, 11] for a Thermal-NIL system. In this paper, E of the resist was manipulated by varying composition of the cross-linking agent and the influence of E of UV resist on the demolding process in UV-NIL was studied by measuring demolding force, the force required to separate mold insert from the molded substrate. As crosslinker content increases from 0 to 49 wt%, both E of the cured resist and shrinkage increase. Demolding force also increases linearly with E. Since shrinkage can apply normal force to the sidewalls of stamp structures, the amount of shrinkage and, therefore, the normal force exerted by it seem to be even of more significance when pattern aspect ratio increases and friction contribution to demolding force gets larger.

2 EXPERIMENT

UV-curable polymeric blends containing polypropylene glycol diacrylate (PPGDA), trimethylolpropane triacrylate (TMPTA), and Irgacure 651 as the base, crosslinking agent and photo-initiator, respectively, were used as a model system for UV resists in this study. Different compositions of PPGDA-based UV resists containing 2 wt% photoinitiator and varying amounts of the crosslinker were all mixed and stirred using magnetic stirrers. The chemical structure of each component used for the UV resist blends is shown in Fig. 1.
PPGDA (n = 7)  

\[
\begin{align*}
H_2C=CH-C\left(OC_{13}H_28\right)_n-O-C=CH=CH_2
\end{align*}
\]

PPGDA

TMPTA  

\[
\begin{align*}
H_2C=CH-O
\end{align*}
\]

\[
\begin{align*}
O-C=CH=CH_2
\end{align*}
\]

TMPTA

\[
\begin{align*}
OCH_3
\end{align*}
\]

\[
\begin{align*}
OCH_3
\end{align*}
\]

Irgacure 651

Fig. 1. Chemical structures of the resist components. PPGDA as the base (oligomer), TMPTA as cross-linker and Irgacure 651 as photo-initiator.

A stamp that is used for UV-NIL and demolding force measurement was fabricated through conventional optical lithography and reactive ion etching. The stamp contains 580 nm deep gratings (or channels) with the width and period of respectively 10 μm and 15 μm. Details of the stamp fabrication can be found in our previous paper [9]. Prior to using the stamp for imprinting, the stamp surface was treated with a fluorinated silane molecule tridecafluoro-1,1,2,2-tetrahydro-octyl-trichlorosilane (C₈H₄Cl₃-F₁₃Si) in the vapor phase using a home-built vacuum chamber in order to reduce adhesion at the stamp/resist interface during demolding.

Imprinting and demolding were carried out in different apparatus. UV-NIL was performed using a commercial nanoimprinter (Obducat 6”) while a modified mechanical tester (MTS Testwork 5) was deployed to measure force/displacement responses during demolding. 1 inch × 3 inch glass slides were used as substrate. The slide glass was treated with oxygen plasma for 15 min at 150 W and 250 mTorr gas flow to enhance its adhesion to the polymer. Almost 20 μL of a UV-curable resist was manually dispensed on the surface of a 1 inch × 1 inch Si stamp mounted on a piece of aluminum with the same size to be fit to the fixtures in our demolding force apparatus. Then the slide glass was concentrically placed on the stamp. Curing was done by a UV lamp at an intensity of 1.8 W/cm² and maximum wavelength intensity at ~365 nm for 10 s while applying pressure at 110 mbar to ensure complete filling of stamp cavities. After imprinting the sample, which is the assembly of aluminum/stamp/resist/slide glass, was transferred to the MTS machine. The aluminum piece was placed into a holder and secured using screws from the sides. The slide glass was also clamped to the upper traverse. Then, tensile displacement at a constant rate of 0.1 mm/min was applied while the force response was measured by a 5000 N load cell. The imprinting and demolding stages are schematically shown in Fig. 2.

In order to investigate the Young’s modulus of our polymers an atomic force microscopy (AFM)-based technique offered by Xu et al. was used [12]. To find the reason for variations in demolding force, polymerization shrinkage was also investigated. To this means, a simple method suggested by Hudson [13] was used. In this method a droplet of polymer is placed on a hydrophobic surface (silicon wafer treated by a fluorinated silane in our case). One picture is taken before shining UV and the sessile volume is measured. Then sessile volume is measured again after shining UV to the polymer to achieve full curing. The volume change with respect to initial volume is the polymerization shrinkage. Procedure was repeated several times and the results were averaged. To ensure that the volume shrinkage was solely caused by shrinkage not evaporation, two pictures were taken of the polymer with a 5 minute interval without any UV shining. The outcome showed no volume change, indicating that no significant evaporation took place within the time required for curing. Fig. 3 shows, as an example, a droplet of one of the polymer blends before and after curing.

Fig. 2. Schematic views of: 1) the stamp mounted on the aluminum piece, 2) dispensed resist, 3) UV curing and 4) demolding.

Fig. 3. Sessile volume change of polymer blend containing PPGDA 70wt%, TMPTA28wt% and Irgacure651 2wt% before and after curing.

The fidelity of imprinted structures was also studied using scanning electron microscopy (SEM) and AFM.
3 RESULT AND DISCUSSIONS

Fig. 4 shows demolding force as a function of the crosslinker content at constant photoinitiator concentration of 2 wt%. As the crosslinker content increases from 0 to 49 wt%, demolding force monotonously increases.

Mainly three factors can influence the demolding force: surface energy, Young’s moduli of the resist and the stamp (by dissipating the force applied in the form of elastic deformation) and also shrinkage by exerting an excess force to the stamp/resist interface. The effect of surface energy and Young’s modulus on surface adhesion (H) between two flat, elastic, cylindrical solids in contact can be theoretically explained by the formula derived by Pollock [14]:

\[
H = \left( \frac{2}{\pi \gamma KR^2} \right)^{\frac{1}{2}}
\]  

(1)

Where H is surface adhesion, \( \gamma = \gamma_1 + \gamma_2 - \gamma_{12} \) is the work of adhesion (\( \gamma_1 \) and \( \gamma_2 \) being the surface adhesion of the two surfaces), K is the composition Young’s modulus calculated from:

\[
\frac{1}{K} = 0.75 \left[ \frac{(1 - \nu_1^2)}{E_1} + \frac{(1 - \nu_2^2)}{E_2} \right]
\]  

(2)

Where \( E_1, E_2, \nu_1 \) and \( \nu_2 \) are Young’s moduli and Poisson’s ratios of two surfaces and R is the effective radius of interface. As one can see, by increasing the composition Young’s modulus (K), surface adhesion increases. Physically the formula implies that, when a normal force P is applied to separate two solids, a portion of this force is dissipated through solids in the form of elastic deformation and the force acting on the interface is the force P minus the dissipated portion of it. Therefore, solids with larger elastic modulus can dissipate more energy and thus require a higher P to separate.

Water contact angle measurements were performed with the UV resists deposited on flat Si surfaces. The results showed virtually the same contact angle of 48.5° ± 2 for all the resists regardless of the composition. This contact angle corresponds to the surface energy of 59.83 mJ/m² based on Antonow method [15]. Fig. 5(a) and (b) respectively show an increase in Young’s modulus and polymerization shrinkage of PPGDA based polymers with increasing crosslinker content from 0 to 49 wt% at a constant photoinitiator concentration (2 wt%).

The reason for the increase in Young’s modulus and polymerization shrinkage is obviously the higher degree of crosslinking through which packed covalent bonds replace loose van der waals bonds between the polymer chains. In the absence of any crosslinker, polymerization proceeds with the breakage of carbon double bonds (vinyl bonds) of PPGDA and formation of acetate groups while photoinitiator acts just as a catalyst. In the presence of the crosslinker (TMPTA) the same mechanism occurs but since TMPTA has three functional groups (PPGDA has two. See Fig. 1), a 3-D network structure of chains will form. Therefore, in the presence of the crosslinker if all the functional groups are activated (or simply all the vinyl bonds are broken and then reacted), more acetate groups should form. Fig. 6 shows Fourier transform infrared spectra for the UV resist with 49% crosslinker content before and after curing. These spectra were normalized with regard to the intensity of carbonyl bond at ~1728 cm⁻¹ which remains unchanged. After curing peaks at 1635 and 1620 cm⁻¹ corresponding to the vinyl group disappear, indicating almost full conversion. Also, comparing the intensity of acetate peaks in PPGDA based polymers in Fig. 7 shows an almost linear increase with increasing the crosslinker. This increase in the degree of crosslinking in turn increases the Young’s modulus (and shrinkage simultaneously) by creating a denser chain network and
hindering the movement of polymer chains when subjected to external forces.

![Fig. 6. FTIR spectroscopy for all the polymers before and after curing shows disappearance of vinyl bonds after curing indicating full conversion](image)

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![Fig. 7. (a) FTIR spectroscopy of the cured polymers, arrow indicates the acetate; (b) Acetate peak intensity peak @ ~1240 cm\(^{-1}\) in FTIR spectroscopy increases by increasing crosslinker concentration.](image)

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Higher Young’s modulus increases the adhesion force based on formula 1. However, at this point it is impossible for us to decouple the effect of Young’s modulus from shrinkage on demolding force.

Through AFM and SEM studies we also observed good pattern fidelity and defect tolerance for all of our imprinted structures even in the absence of any crosslinker in the polymer solution. Relaxation manifested itself as an increase in the length of imprinted pattern’s protrusions while the magnitude of relaxation did not depend on crosslinker content.

4 CONCLUSION

We measured the force required to separate the imprinted pattern on a glass substrate from a Si stamp treated by a silane molecule for UV-curable polymer blends containing PPGDA, TMPTA and as respectively the base, crosslinking agent and photo-initiator at different concentrations of the crosslinker. The main three factors affecting the demolding force; polymerization shrinkage, Young’s modulus and surface adhesion, were discussed. Increasing crosslinking agent content from 0 to 49 wt% increases the Young’s modulus and polymerization shrinkage of PPGDA based polymers while it has no effect on surface energy. The increase in Young’s modulus and shrinkage in turn almost doubled the demolding force.

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REFERENCE
