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Controlling Mold Releasing Propensity—The Role of Surface Energy and a Multiple Chain Transfer Agent

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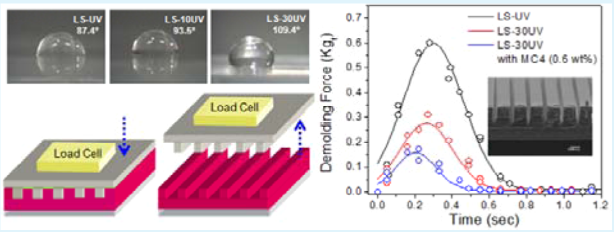
ABSTRACT: As the desired feature size of mold-assisted lithography decreases rapidly efficient demolding process becomes more challenging due to strong adhesion between polymeric resists and fine-featured molds. We synthesized new macromolecular additives and investigated the effects of surface energy and contraction of resist materials on demolding propensity by monitoring the adhesion force between the resist and the applied mold. The resist's surface energy was controlled, as inferred from water contact angle measurements, by chemically modifying its hydroxyl functionality. The resist's degree of volume shrinkage during the photocuring procedure was also controlled by mixing in a newly developed chemical that has a multiple radical chain transfer capability. The adhesion force was proportionally reduced as the surface energy of the resist materials decreased and as the volume shrinkage was reduced. When the volume shrinkage control was applied in conjunction with the low surface energy resist material (LS-30UV), we obtained an optimized condition requiring a minimum force for releasing the mold from the cured resist layer.



KEYWORDS: *radical chain transfer, multichain transfer agent, UV imprint lithography, adhesion, transparent UV-cure resin, synthesis*

INTRODUCTION

Demands for developing a cost-effective pattern fabrication method to supplant traditional photolithography have led to the development of several direct pattering techniques including nanoimprint lithography (NIL),[1−5] microinjection molding (MIM),[6,7] step-and-flash imprint lithography (SFIL),[8,9] additive soft lithography,[10,11] and microtrasnfer molding.[12] Each of these techniques uses a mold with a protruding/recessed surface that is transferred onto the surface of a resist material by physical pressure, after which the mold is released. One of the most common problems that is encountered during adoption of mold-assisted lithography is the tendency for the resist material to adhere to the mold surface during the demolding process, resulting in defects. In addition to damaging the transferred pattern, residual resist on a mold surface can reduce the mold lifetime by disrupting the fidelity of the designed patterns.[13,14] These are critical bottlenecks to the application of newly devised molding systems to large area mass production. To relieve these problems, various modifications have been proposed such as mold surface treatment with a self-assembled monolayer (SAM)[15−17] or utilization of low surface energy materials.[18−20]

(Transparent) UV-curable resins have great potential when combined with direct patterning methods. They can provide patterns having resistance to chemical or mechanical substrate etching while acting as a mask. They can also serve as functional layers in electronic devices such as optical films,[21] column spacers or color filters for liquid crystal displays (LCD),[22] and as sealing layers for electronic devices.[23] Unfortunately, employing UV-curable resins as imprintable resist materials has some limitations. During the UV curing process volumetric contraction happens because chain ends, which occupy a relatively larger free volume, are consumed. This results in an interdigitated, friction-interlocked interface between the mold and the cured resist material. Although molds are typically made with low surface energy materials such as fluoropolymers or polydimethysiloxane (PDMS), the strongly engaged mold/resist can cause a high adhesion force that complicates mold release.[24] The adhesion between the mold and the resist materials is inextricably related with the demolding feasibility, and finally, with a generated pattern's quality. In this contribution, we measured the adhesion force during mold release as a function of the surface energy and the degree of contraction of a UV-curable resin. Since the surface energy of organic materials is closely related with the functional groups that they contain, the hydrophilic moieties of a UV-curable resin were partly modified and the resulting surface energy change was characterized by means of water contact angle measurement. To control the degree of contraction, the number of chain ends was regulated with a novel chain transfer agent having multiple radical transfer units. The multiple CT

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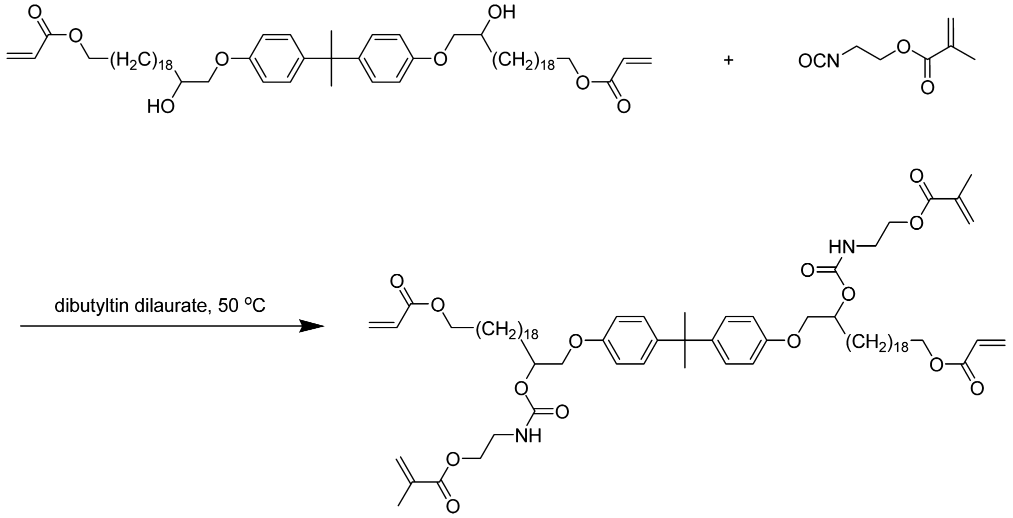
Scheme 1. Chemical Structure of Bisphenol a Diacrylate and Its Modification Procedure



agent generates additional chain ends and results in a relatively small volume change during the UV curing process.

■ EXPERIMENTAL SECTION

Materials. UV-curable resin, LS-UV, was given by LMS Corporation of South Korea and used as received. 3-Benzylsulfanyl thiocarbonyl-sulfanyl propionic acid was synthesized in a previously described manner[25] and all other starting materials were purchased from commercial suppliers (Aldrich and Fisher Sci.) and obtained compounds were fully characterized with ^{1}H NMR and GC-mass.

General Procedure of UV-Curable Resin (LS-UV) Modification. Under Ar condition, 10 g of LS-UV and 2-isocyanatoethyl methacrylate were mixed. After adding a catalytic amount of dibutyltindilaurate, the mixture was stirred for 4 h at 50 °C. After confirming the reaction by means of infrared spectroscopy (IR) and differential scanning calorimetry (DSC) after curing the mixture by UV irradiation, it was used for adhesion measurements without any further purification.

LS-10UV. 2-isocyanatoethyl methacrylate (0.16 g, 1.01 mmol) was used and the reaction was judged both from the disappearance of N═C═O stretching (2270 cm^{-1}) in IR spectrum and from no heat transition in DSC.

LS-30UV. 2-isocyanatoethyl methacrylate (0.47 g, 3.03 mmol) was used and the reaction was judged as similarly as LS-10UV did.

3-(Tetrahydro-2H-pyran-2-yloxy)propane-1,2-diol (1). Ten grams (108.6 mmol) of glycerol was homogeneously stirred to DMF/THF (1 mL/25 mL). 7.5 mL (82.7 mmol) of 3,4-dihydro-2H-pyran (DHP) and 0.16 g (0.8 mmol) of *p*-toluenesulfonic acid monohydrate were added to the solution at 0 °C and then, stirred for 2 h. After washing the mixture with $NaHCO_3$ solution, it was extracted with ethyl acetate and solvent was evaporated in vacuo.Compound **1** was purified by silica gel column chromatography (yield; 83%). ^{1}H NMR (300 MHz, $CDCl_3$) 1.55−1.57 (m, 4H), 1.76−1.82 (m, 2H), 3.52−3.81 (m, 7H), 4.54−4.56 (m, 1H) and *m*/*z* EIMS 177.

Compound 2. 6.1 g of DCC (29.6 mmol) and 0.09 g (0.7 mmol) of DMAP were added to the solution of 3 g (14.1 mmol) of compound **1** and 3-benzylsulfanyl thiocarbonyl-sulfanyl propionic acid (7.68 g, 28.2 mmol) in 20 mL of CH_2Cl_2 at 0 °C. After stirring for 3 h, hexane was poured into the reaction mixture to precipitate, and generated urea was filtered off. After evaporating solvent, silica gel column chromatography gave 8.7 g of a yellow gel (yield; 90%).^{1}H NMR (300 MHz, $CDCl_3$) 1.55−1.91 (m, 6H), 2.79−2.83 (m, 4H), 3.52−3.67 (m, 6H), 3.72−3.81 (m, 2H), 4.21−4.29 (m, 1H), 4.37−4.42 (m, 1H), 4.57−4.62 (m, 1H), 4.60 (s, 4H), 5.22−5.29 (m, 1H), 7.26−7.33 (m, 10H) and *m*/*z* EIMS 685.

Compound 3. 8.5 g (12.4 mmol) of compound **2** was deprotected by stirring with 5 mL of 2N HCl in THF/CH_3OH (10 mL/10 mL). The mixture was washed with $NaHCO_3$ solution and extracted with ethyl acetate. 5.9 g of compound 3 was obtained after purification with silica gel column chromatography (yield; 80%). $_1$H NMR (300 MHz, $CDCl_3$) 2.79−2.84 (m, 4H), 3.62−3.66 (m, 4H), 4.17−4.24 (m, 5H), 4.61 (s, 4H), 7.26−7.35 (m, 10H) and *m*/*z* EIMS 601.

MC4 (Compound 4). To the mixture containing 5.8 g of compound **3** (9.7 mmol) and 2.8 mL (20.0 mmol) of triethylamine in 30 mL of CH_2Cl_2, was 0.96 mL (11.9 mmol) of acryloyl chloride added at 0 °C. After additional stirring for 2 h, the mixture was washed with NH_4Cl solution and extracted with ethyl acetate. 4.9 g of yellow oily compound **4** was obtained with 78% yield from silica gel column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) 2.78−2.83 (m, 4H), 3.60−3.64 (m, 4H), 4.18−4.28 (m, 2H), 4.36−4.41 (m, 2H), 4.60 (s, 4H), 5.31−5.36 (m, 1H), 5.88 (d, 1H, *J* = 10.4 Hz), 6.12 (dd, 1H, *J* = 17.2, 10.8 Hz), 6.43 (dd, 1H, *J* = 17.2, 1.2 Hz), 7.26−7.32 (m, 10H) and *m*/*z* EIMS 653.

Specific Volume Change Measurement. The specific gravity of the resist was directly measured before UV curing, and the reciprocal value of the obtained specific gravity was used as the specific volume of the uncured resist. After casting the resist on PDMS film with a doctor blade, the obtained resist film was fully UV-cured by means of a high pressure Hg lamp (14 mL/m2 s from i-line, 300 mJ). Then, the cured resist was detached from PDMS film in a water bath, and its volume and weight were determined after applying 1-min ultrasonication to remove air bubbles at the surface of the cured resist. The specific gravity of the cured resists was measured 3 times under the same condition, and the average value of the obtained data was used as the specific volume of the cured resist.

Swelling Ratio and Cross-Linking Density. After casting the resist on PDMS film with a doctor blade, the obtained resist film was fully UV-cured under high pressure Hg lamp (14 mL/m^2 s from i-line, 300 mJ). Then, the cured resist was detached from PDMS film and soaked in THF for 1 day under ambient condition. The wt % swelling ratio was calculated based on the weight change before and after the THF treatment. Finally, the cross-linking density was determined based on Flory's network theory[26] with 0.56 of solvent interaction parameter.

Adhesion measurement. To provide a uniform adhesion, we fixed the substrate (PET film) with double sided tape on top of the sample holder. After coating resist materials by means of a doctor blade (∼ 200 μm), the patterned mold was pressed into it and the resist layer was fully photocured with a high pressure Hg lamp (14 mJ/m^2 s from i-line, 300 mJ). Then, the adhesion between the photocured resist layer and the mold was monitored via a load cell while releasing the mold from the substrate. In this experiment, the contact surface area of the applied mold having stripe patterns was 225 mm^2, and the

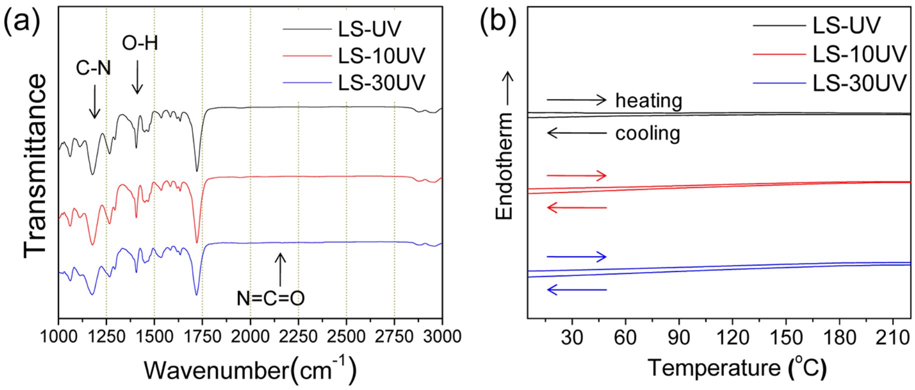


Figure 1. (a) IR spectroscopy and (b) DSC thermogram of UV-curable resin containing chemically modified bisphenol A diacrylate.

dimensions of the stripe pattern were 188 μm (height) × 132 μm (width) × 37 μm (space).

Water Contact Angle Measurement. A resist layer (30 μm) was prepared on top of bare glass and photocured under a high pressure Hg lamp (14 mJ/m^2 s from i-line, 300 mJ). After placing water doplet (5 μL) on the fully cured resist film, the image was captured quickly (less than 5 s) to minimize an experimental error from the evaporation of the placed water. In order to draw circle, three different points were made at the surface of the water droplet from the captured image, and water contact angle was finally extracted. Same procedure was performed at six different positions with same sample and obtained water contact angles were averaged.

■ RESULTS AND DISCUSSION

To investigate the relationship between the surface energy of a UV-curable resin and its adhesion to the mold as a resist material, we adopted a commercially available UV-curable resin (LS-UV). LS-UV is an optically transparent liquid which consists of 50 wt % of a bisphenol A diacrylate oligomer (molar mass; 990 g/mol, n = 18), in addition to a urethane diacrylate oligomer, a photoinitiator and no solvent. As shown in Scheme 1, the bisphenol A diacrylate oligomer contains two hydroxyl groups (OH) which enhance molecular surface energy, and we partially modified them with 2-isocyantoethyl methacrylate to control the surface energy of LS-UV. Since this modification method does not yield any byproduct the reaction mixture could be directly used for further investigation without any purification procedure. Ten mol % (LS-10UV) and 30 mol % (LS-30UV) of the hydroxyl groups in the bisphenol A diacrylate oligomer were respectively modified, and the degree of reaction was determined by means of infrared (IR) spectroscopy and differential scanning calorimetry (DSC) after curing the reaction mixture. As shown in Figure 1(a), we could see in IR spectroscopy that the O−H bending vibration around 1370 cm^{-1} diminished and the N=C=O stretching vibration (2100−2270 cm^{-1}) of 2-isocyantoethyl methacrylate completely disappeared in all samples, indicating that the added modifier, 2-isocyantoethyl methacrylate, is completely reacted with the hydroxyl groups of the bisphenol A diacrylate oligomer. In addition, the C−N stretching (1170 cm^{-1}) had broadened, due to the newly generated urethane linkage, even more than untreated LS-UV which exhibits some C−N stretching because of its original urethane modified oligomercomponent. Thermal analysis did not revealany transitions, as shown in Figure 1(b), after UV curing of LS-UV, LS-10UV and LS-30UV, indicating that no residual monomer, such as unreacted reagent, existed. Based on the results of IR spectroscopy and DSC, we could confirm that the chemical modification was successfully carried out as desired. To investigate the change of surface energy accompanying the hydroxyl group modification, water contact angle (CA) measurements, which have an inverse relationship with the surface energy,[27] were taken. As depicted in Figure 2, the water CA increased from 87.4° (LS-UV) via 93.5° (LS-10UV) to 109.4° (LS-30UV) as more hydroxyl groups had been modified. Since the hydroxyl group is one of the strongest hydrophilic moieties (which increase molecular surface energy), the results are reasonable.

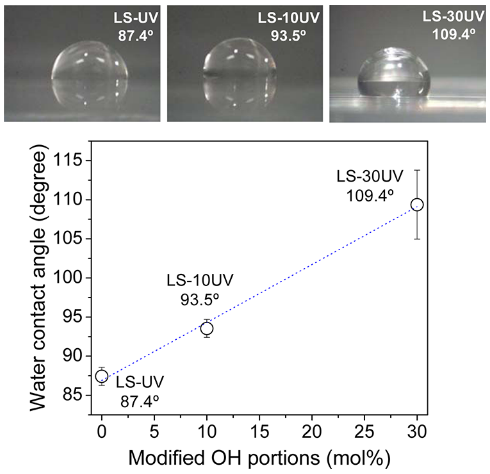
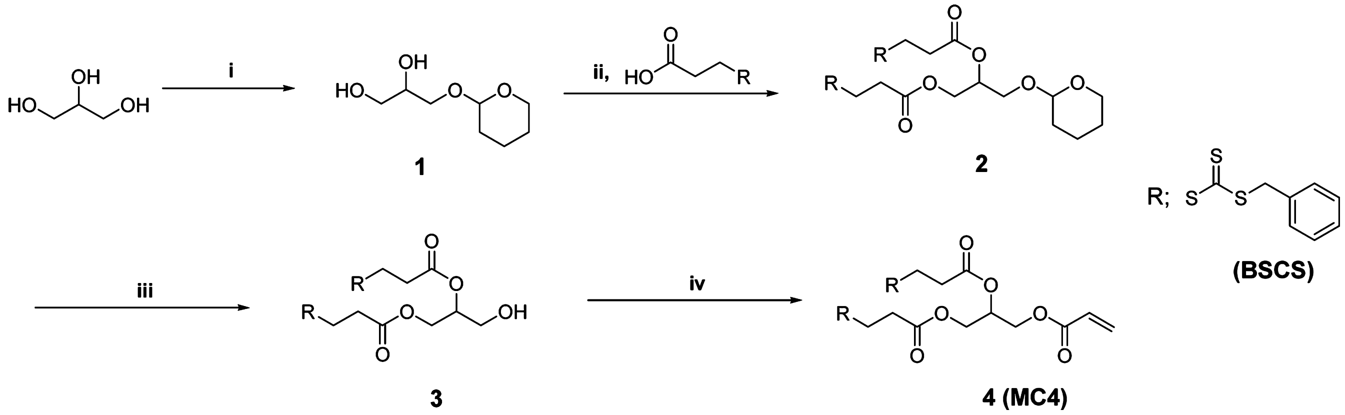


Figure 2. Water contact angle of UV-curable resins containing chemically modified bisphenol A diacrylate.

Although the surface energy of a resist strongly affects the demolding property in the direct pattern imprinting process, the degree of volume shrinkage of the resin during the curing could be more determinant because the volume shrinkage can strongly interlock the patterned resin and the applied mold. Recently, the effects of various parameters (such as light intensity, initiator concentration, chemical structure of the monomer, and presence of chain transfer agent) on the kinetic chain length of the UV cured resin and ensuing volume shrinkage have been studied.[28] The shrinkage of the cured UV patterns decreased as the kinetic chain length decreased because a smaller chain length results in a larger free volume coupled with a large number of chain ends. In addition, cross-linking through ring-opening polymerization of expoxide rings was investigated to regulate the shrinkage because such ring-opening polymerization produces an equivalent number of

Scheme 2. Synthetic Procedure of Multiple Chain Transfer Agent[a]



[a](i) DHP, pTsOH.H_2O, DMF/THF, 0 °C, 2 h; (ii) DCC, DMAP, CH_2Cl_2, 0 °C, 3 h; (iii) HCl, THF/CH_3OH; and (iv) acryloyl chloride, triethylamine, CH_2Cl_2, 0 °C, 2 h.

Table 1. Characterized Properties of UV-Curable Resins

samples	specific volume (cm^3/g) before UV cure	after UV cure	change (±2.0%)	contact angle (de)	swelling ratio	cross-linking density (mol/cm^3)[a]	demolding force (Kg_f)
LS-UV	0.762	0.631	17.2	87.4	1.08	15.14	0.58
LS-30UV	0.744	0.560	24.7	109.4	1.03	25.37	0.28
LS-30UV MC4(0.3 wt %)	0.746	0.605	18.9	110.5	1.07	16.44	
LS-30UV MC4(0.6 wt %)	0.750	0.679	9.5	112.1	1.14	10.16	0.15

[a]$\nu_x = (\ln(1 - q^{-1}) + q^{-1} + \chi_1 q^{-2})/(v_1(q^{-1/3}))$ (swelling ratio); q (swelling ration), V_1 (solvent molar volume), and χ_1 (interaction parameter).

chain ends, which minimizes the shrinkage by maintaining the free volume the chain ends occupy.[29] However, developing a specific cross-linker to regulate the volume shrinkage has a limited practical value because cross-linkers largely affect the properties of the cured resin, such as chemical resistance, thermal stability, optical properties, and mechanical properties. Thus, a strategy that effectively controls the volume contraction without altering the general properties of the pristine resin would be ideal as a general solution. In this regard, devising a radical chain transfer (CT) agent having multiple chain transfer (multi-CT) units would be a promising way to regulate volume contraction during UV imprinting lithography. Chain transfer agents have been used to create highly branched polymers.[30,31] Recently, thiol additives have been investigated as a chain transfer agent in methacrylate-based dental restorative materials to reduce stress at the bonded interface.[32] Herein, to restrain the contraction resulting from the decrease of chain ends during the UV curing process, we designed a new multi-CT agent containing the 3-benzylsulfanyl thiocarbonyl-sulfanyl (BSCS) moiety. The BSCS group is a common CT agent used in the living radical polymerization, reversible addition–fragmentation chain transfer (RAFT).[25,33] As shown in Scheme 2, MC4 which has two BSCS and one acrylate moieties was successfully synthesized and fully characterized by means of NMR and GC-mass. Detailed synthetic conditions are summarized in the experimental section. In MC4, the BSCS groups were introduced for radical chain transfer which produces a multibranched network. The acrylate moiety was adopted to embed MC4 molecule in the resist matrix by participating in the UV curing as evenly as oligomers consisting of LS-UV do. We changed the MC4 content in LS-30UV and measured the specific volume change after UV photocuring to confirm MC4's effect on regulating the degree of contraction. As summarized in Table 1, LS-30UV, which was chemically modified to control the molecular surface energy, exhibited much more shrinkage (24.7%) than LS-UV (17.2%). We believe that this is mainly due to the methacrylate units which were introduced from the modification reaction of the OH group in bisphenol A diacrylate. Because the newly generated methacrylate groups also participate in UV curing, increasing their population could induce a relatively larger loss of chain ends compared to LS-UV, resulting in aggravated contraction after the UV curing procedure. When MC4 was added into LS-30UV, the degree of contraction after UV curing decreased. 0.3 wt % of MC4 in LS-30UV provided contraction similar to the original LS-UV and, when its contents increased up to 0.6 wt %, LS-30UV showed less than 10% contraction after UV curing. The addition of MC4 to LS-30UV suppressed shrinkage during the UV curing procedure, but the surface energy, judged from water contact angle, stayed at a similar value of LS-30UV because its MC4 content was too small to produce a noticeable change of molecular surface energy. We investigated the effect of MC4 addition on the cross-linking density of LS-30UV. As summarized in Table 1, the LS-30UV containing 0.6 wt % MC4 showed 14% swelling in a good solvent, tetrahydrofuran (THF), whereas the pristine LS-30UV swelled only 3%. Our cross-linking density calculation with these swelling ratios, based on Flory's network theory, showed that the cross-linking density decreased from 16.44 mol/cm^3 of the pristine LS-30UV to 10.16 mol/cm^3 by 0.6 wt % MC4 addition.[26] The results are reasonable because as designed MC4 induces multiple chain transfers to form many more free chain ends that are not

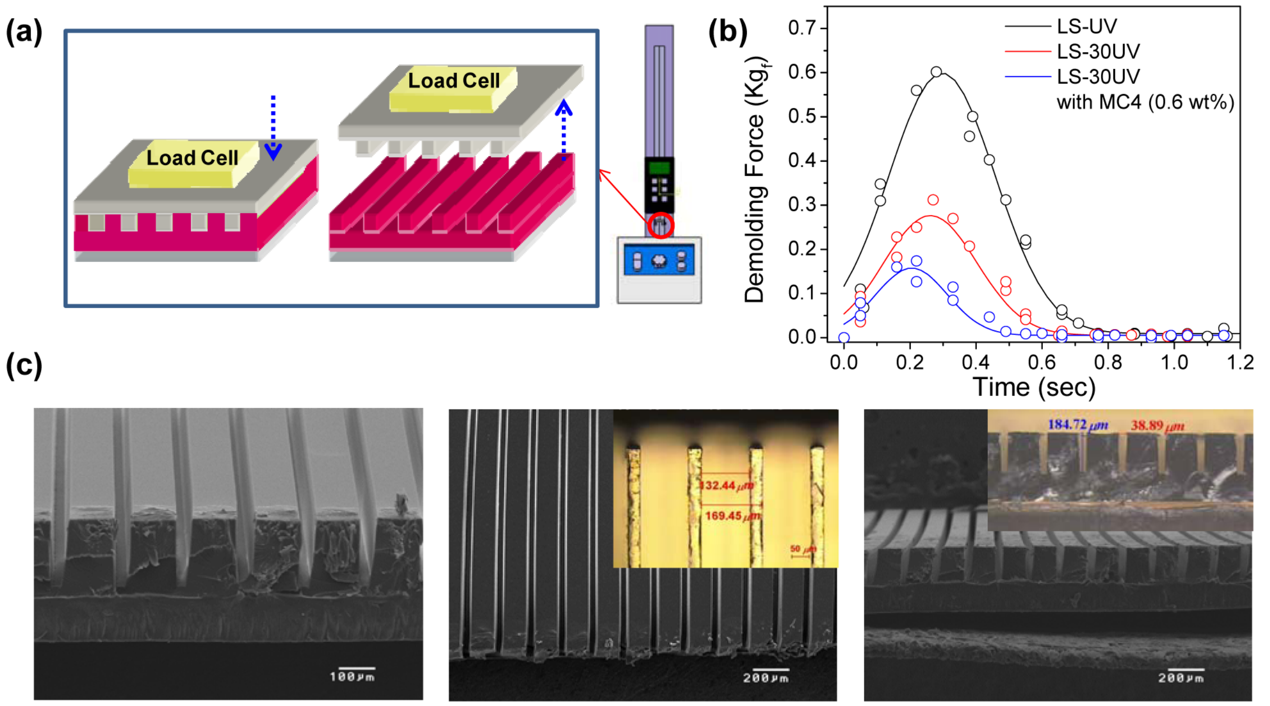


Figure 3. (a) Schematic diagram of the adhesion measurement tool and (b) obtained demolding force profile. (c) Pattern features produced during the adhesion measurement; insets indicate the dimensions of the applied mold (middle) and the obtained patterns (right).

involved in cross-linking.To investigate the effect that contraction has on adhesion between the mold and cured resist, we selected LS-30UV containing 0.6 wt % MC4 for adhesion force measurement.

To measure the adhesion force during the demolding process, we fabricated a hard mold with 6:4 copper/brass containing strip type pattern (188 μm (height) × 132 μm (width) × 37 μm (space)). As depicted in Figure 3a, a load cell (AD4935−50N) which can measure up to 50 N with 0.01 N resolution was installed on top of the mold and the required force was recorded by releasing the mold from cured resists. Demolding force was measured several times under the same conditions and characteristic adhesion data points were collected only when no pattern fracture happened in order to reduce additional experimental error. Under our data sampling setup (scan rate: 10−50 Hz), the obtained forces exhibited a Gaussian profile and their maximum value was considered as the adhesion force between the mold and the cured resist. The effect of the surface energy on the adhesion force was investigated by comparison between LS-UV and LS-30UV and similarly, the contraction or its combined influence with the surface energy was characterized with the contraction regulated LS-30UV with MC4 (0.6 wt %). As shown in Figure 3b and Table 1, LS-UV,which has a high surface energy, exhibited the highest adhesion force with the mold (0.58 kg$_f$) and, when the surface energy was reduced (LS-30UV), the adhesion strength (0.28 kg$_f$) was dramatically reduced to about half of that of LS-UV. Furthermore, whenthe degree of contraction was modulated with MC4 in LS-30UV, the demolding procedure required a minimum force (0.15 kg$_f$). On the basis of our results, the surface energy and the degree of contraction clearly influence the adhesion force with the applied mold and further, when they are properly controlled together we expect to obtain an optimum demolding condition. Figure 3c shows representative patterns which were used for the measurement of demolding force.

CONCLUSION

In summary, the effect of surface energy and contraction of resist materials on the demolding process was characterized by measuring the adhesion force between the resist layer and the mold. The surface energy of the resist resin was controlled by modifying the resist's hydroxyl groups and its change was monitored with water CA measurement. Reduced surface energy in the cured resist was obtained when a larger portion of OH groups were modified, resulting in a reduced adhesion with the mold compared to the unmodified resist. To regulate the degree of contraction during the UV curing process, a novel multi-CT agent containing two BSCS moieties was synthesized, and the specific volume change was measured after UV curing. The multi-CT agent effectively suppressed the degree of contraction during the UV curing procedure of the cured resist. When volume contraction control was combined with the low surface energy resist we obtained an optimized condition requiring a minimum force for releasing the mold from the cured resist layer. Our result indicates that the molecular surface energy and the degree of contraction of resist materials evenly affect the adhesion with the mold and they should be controlled together to realize a better demolding process. The presented results can be adapted to other polymer modification/formulation for more efficient mold-assisted lithography. As the feature size of mold-assisted lithography gets smaller the developed strategies become more critically important.

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Notes

The authors declare no competing financial interest.

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