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Nanometer-level high-accuracy molding using photo-curable silicone elastomer by supressing thermal shurinkage

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Abstract

Although so-called labs-on-a-chip or micro total analysis systems (micro TAS) fields hold high promise for applications in many fields, conventional fabrication processes based on the semiconductor industry such as photolithography have limitations in terms of productivity. Silicone elastomers are widely used for micromodeling and offer biocompatibility and chemical stability, but they are generally thermosetting and undergo unacceptable levels of shape deformation during curing. In this study, a photocurable silicone elastomer that has recently become commercially available was examined and its basic optical, mechanical, and other related characteristics, along with its shape transfer capabilities, particularly its nanostructure replication characteristics, were measured in comparison with those of a representative existing thermosetting silicone elastomer. As a result, the photo-cured elastomer was shown to be superior to existing heat-cured silicone elastomers to have mechanical strength approximately three times higher tear strength, and was shown as same as in optical transmittance extending from the near-IR to the near-UV regions. In addition, it was shown that the elastomer is sensitive to light in a wide range of wavelengths from 254 to 600 nm with no large difference in curing characteristics, indicating that curing can be performed under a variety of common forms of illumination. Most importantly, the photocured elastomer provided extremely high replication accuracy due to its thermal shrinkage less than 0.02%, compared to 2.91% in the heat-cured elastomer.

Keywords: Polydimethylsiloxane, photocurable silicone elastomer, microprocessing, molding

1. Introduction

Microchips referred to as labs-on-a-chip or micro total analysis systems (μTAS) have become a focus of intense research. These chips are fabricated by simultaneously downsizing and integrating all of the micro/nanocomponents necessary for a given functions of reaction or analysis, including both fluid-control elements such as pumps, valves, etc. and functional elements such as heaters, separation structures, etc. The chips hold high promise for applications in many fields, including analytical chemistry, life science, and medicine.[1-5] Their first major application was in the form of bioanalytical chips for DNA sequencing and protein analysis,[6-9] but the trend has more recently shifted to other areas, with medicine-engineering collaboration field.[10] This trend is rapidly growing in point-of-care, personalized medicine, and medical implant devices, and in an expanding range of component materials.[11-13]

In this context, seed research for microprocessing technology and materials that will enable effective fabrication of the related devices and systems has become a fundamental requirement. The microchips have been fabricated by photolithography and other microprocesses adopted from the semiconductor industry, but those fabrication processes involve certain limitations: 1) they require large-scale equipment based on vacuum processing, 2) they involve long takt times, and 3) their batch sizes are constrained by the size of the vacuum equipment and productivity is therefore too low, particularly for the many medical applications requiring disposability.[10, 14] Fabrication processes with higher productivity at lower cost have become a key goal for industrialization. In fabrication materials, the goals that have emerged include lower cost together with low (if possible, no) biotoxicity and thus biocompatibility and with functional properties such as low adsorption of biomaterials.

In the research to achieve these goals, attention has turned to technologies such as embossing, molding, and other processes to facilitate mass production and reduce costs.[15, 16] Several of these are nanoprinting and injection molding, which has already been in use for some time.[17] In laboratory prototyping, silicone elastomers are widely used for micromodeling because of their good moldability and the relatively simple, low-cost equipment required,[16, 18, 19] and also because of their superiority to other polymers in biocompatibility and chemical stability, despite their characteristic disadvantages as soft elastomers.[20, 21] Silicone elastomers generally are thermosetting and therefore require heating for effective curing.[18] Their characteristic elasticity and deformability as elastomers facilitate the transfer of fine structures over large surface areas without mold damage. On the other hand, as thermosetting resins, they undergo large shape deformation under the thermal residual stress imposed by heat curing, which substantially reduces their replication accuracy.[22, 23] For micro- and nano-devices requiring accuracies on the micrometer (10^{-6} m) and nanometer (10^{-9} m) scale, even 1% shrinkage usually exceeds permissible tolerances. Research has generally focused on incorporating allowances for the dimensional changes induced by this thermal residual stress into the device design, but this has proved difficult and finding a solution to this problem has become a bottleneck for practical development of micro- and nano-devices, particularly nanostructure fabrication from silicone elastomers.

In the present study, we propose and investigate an alternative solution to this problem. To facilitate high-accuracy nanoscale replication, we propose the use of a photocurable silicone elastomer recently placed on the market, which eliminates the need for heat curing. It was investigated that its basic optical, mechanical, and other related characteristics, and then quantitatively assess its shape transfer capabilities, particularly its nanostructure replication characteristics in comparison with those of a thermosetting silicone elastomer.

2. Experimental

In this study, X-34-4184 (Shin-Etsu Silicone) was used as the photo-initiative silicone elastomer and Sylpot 184 (Dow Corning Toray Co.) as representative of existing thermosetting silicone elastomers. Light exposure activates the catalyst, and then the polymerization will start and dominated by the activity catalyst, in the case of X-34-4184. It means the polymerization itself is not progressed by photon energy, however the mechanism of polymerization should be almost same as the Silpot 184. The difference is photo-initiative properties and the very high activity of catalyst. Silpot 184 is only partly cured at room temperature resulting in very soft, whereas X-34-4184 is almost fully cured and much faster (hundreds times or more). That means X-34-4184 requires much less thermal energy compared with Silpot 184. Therefore, we called X-34-4184 as photo-curable PDMS in this paper as contrastingly discuss between them.

As the light source for the photosetting, we used a low-pressure mercury lamp (Multilight: ML-251, Ushio Inc.) equipped with a 365 nm wavelength bandpass filter. For the measurement of optical transmittance, we used a spectrophotometer (V-660, JAS Co), and for the Fourier transform infrared spectrophotometry (FTIR), we used an FTIR measurement system (FT/IR-4100ST, Jasco Corp.). We used a durometer (Hardmatic HH-332, Mitutoyo) to measure the elastomer hardness, as represented by Shore A hardness. To evaluate the mechanical strength, we formed dumbbell-shaped samples in accordance with JIS K6251-7 and measured their tensile strength using a force gauge (Z2-200N, Imada Co., Ltd.). The surface morphology and shrinkage was directly evaluated by the visualized image with a 3-dimesional confocal laser microscope (VK-X200, Keyence Co.)

3. Results

3.1 Photocuring characteristics

We determined the light exposure dose needed to cure the X-34-4184 silicone elastomer by measuring the Shore A hardness evaluated under exposure to 365 nm-wavelength UV light. The results are shown in Fig 1. In this figure, the blank region in the first few minutes represents the time when the elastomer was still in liquid form and its hardness therefore could not be measured. Therefore, the figure shows the data obtained from the time it became possible to measure the Shore A hardness. Figure 2 shows typical results of our measurement of the change in viscosity of the elastomer while still in liquid form, corresponding to the blank region in Fig. 1.

As shown in Fig. 1, the rate of hardening of the elastomer initially varied with the light-exposure dose however by 30 min after exposure attained a Shore A hardness near 4.5 for all doses and remained constant thereafter. This result shows that, X-34-4184 silicone elastomer is extremely sensitive and reciprocity-law-failure in its response to light exposure. As shown in Fig. 2, immediately following the exposure dose of 1.87 J/cm^2 also shown in Fig. 1, the rise in viscosity was accompanied by a temperature rise of several degrees Celsius, apparently caused by heat evolution while curing in the liquid form. This rise is presumably too small to impose a thermal stress into the cured silicone elastomer. It may also be noted that this period of several minutes in liquid form following exposure would be highly advantageous in mass production as it would allow sufficient time for mold casting of the exposed elastomer.

In the range tested, the results also showed that the elastomer is sensitive to light in a wide range of wavelengths, extending from 254 to 600 nm, with no large difference in curing characteristics even under exposure to visible light. This indicates that its curing can be performed under fluorescent lighting, sunlight, or other common forms of illumination, which would allow a substantial reduction in equipment cost. It also indicates, however, that care in its handling will be needed to ensure its conformity to delicate material, even in a yellow room.

Although the primary purpose of this study was to investigate the possibility of using this elastomer to eliminate the need for high-temperature curing and thus minimize thermal stress, we also investigated the dependence of its curing characteristics on process temperature in view of the possibility that heating the elastomer might provide other significant advantages such as shortened curing times under heating, in applications where the effects of thermal stress would pose no problem. Figure 3 shows typical curing properties found with a light exposure dose of 1.87 J/cm^2 at process temperatures of 20 (as shown in Figure. 1), 70, 110, and 150˚C. These results showed that the curing properties are strongly nonlinear with temperature. If the temperature is more than 70 ºC, the curing finishes very quickly, thus we found no large differences in either curing rate or hardness beyond that temperature. In summary, curing the elastomer at 70˚C or higher substantially increased the curing rate as compared with that at room temperature, and thus reduced the curing time. The curing rate may therefore be a key parameter for improvements in productivity.

3.2 Mechanical characteristics

We investigated the physical strength of the cured elastomers, as a representative indication of their tensile strength. The tensile strength of viscoelastic bodies such as elastomers generally varies with the rate of elongation, and we therefore performed the measurement in a quasi-static state, at a tensile rate of 1 mm/s or lower. Figure 4 shows the results after curing with an exposure dose of 1.87 J/cm^2 at a) 20˚C and at b) 110˚C of X-34-4182, in comparison with c) Sylpot 184 after thermal curing at 110˚C for 1 hour. As shown, X-34-4101 exhibited a higher tensile strength after curing, and its strength after 100 ºC curing was about 2 or less times high, and after room-temperature curing was 4 or more times high as that of Sylpot 184, which clearly indicates that it is superior to Sylpot 184 in mechanical characteristics.

3.3 Spectral characteristics

Figure 5 shows the results of the FTIR measurements of the cured X-34-4184 and Sylpot 184. No specific information on their molecular structures and additives is publicly available as they are commercial products, but the FTIR spectrum found for the X-34-4184, with its basic structure being polydimethylsiloxane (PDMS), is almost identical to that found for Sylpot 184. The only difference between the two elastomer spectra is the strong absorption from 2280 to 2400 cm^{-1}, which is present in the X-34-4184 spectrum but almost absent from the Sylpot 184 spectrum. This absorption would be most likely attributable to the X-34-4184 photocrosslinking agent. The transmitance spectrum of X-34-4184, as shown in Figure. 6, exhibits a strong peak around 250 nm, which again would be most likely attributable to its photocrosslinking agent. It must be noted, however, that this remains in the realm of conjecture because of the confidentiality of the molecular structure and other aspects of the crosslinking agent. Figure 6 shows that X-34-4184 exhibits good transmittance in the UV region of 300 to 400 nm, which indicates that it is superior to existing heat-cured elastomers such as Sylpot 184 as a material for optical transparency.

In summary, the X-34-4184 spectra exhibit characteristic peaks presumably attributable to its photocrosslinking agent, but are otherwise nearly identical to those of Sylpot 184, and it may therefore be expected to have physical properties nearly the same as those of Sylpot 184. The results also demonstrate that its near-UV transmittance is superior to existing materials and taken together indicate that it will be upwardly compatible with existing materials in transparency**.**

3.4 Characteristics of nanostructure replication

We evaluated that replication accuracy with X-34-4184 expected to be higher than with Slypot184, caused by an extremely small shrinkage due to its non-thermal curing effect. Figure 7 is a schematic of the general replication procedure. Broadly speaking, the procedure comprises three main steps: (a) casting, (b) curing, and (c) mold release. The procedure with the photocurable elastomer differs from that with the heat-curing elastomer only in the use of light exposure rather than heating in step (b). The photocuring conditions used here may be regarded as typical and consisted of exposing the sample at 20°C room temperature, 365 nm wavelength, and dose 1.87 J/cm^2, and then letting it cure for several hours to ensure hardening. The hardened sample was then tested for replication accuracy. For comparison with heat-cured elastomers, we cured Sylpot 184 at 100˚C, and submitted it to the replication testing. The results shown in Figure. 8 are typical example visualized by the 3-dimensional confocal laser microscope. The mold used in the replication was shaped as shown in Figure. 8(a) and consisted of a Si wafer with photoresist (SU-3035, Microchem. Inc.) structures.[24] Figure 8(b) shows the result of the shape transfer to the photocurable silicone elastomer X-34-4184 by the procedure shown in Figure. 7. As may be seen from the shape hues representing the height of the structures (with warmer hues indicating greater height), the replication results in a 180º rotation between the master mold and the X-34-4184. The image provides qualitative confirmation that the various complex micrometer-order shapes have been accurately transferred.

Figure 9 shows the results of a nanoscale replication performed to evaluate the transfer accuracy. The image in Figure. 9(a) shows the nanometer-sized pattern formed on the quartz-glass mold master by electron-beam patterning and plasma etching. Figures 9 (b) and (c) show the results of the pattern replication with X-34-4184 and Slypot184, respectively. The pattern depth is 200 nm, the line widths in the four groups from left to right are 200, 300, 500, and 800 nm, and the width to space ratio in all four groups is 1:3.

The differences between the shapes on the mold master and the replicates were evaluated by the 3-D confocal laser microscopy. The results showed that a shape shrinkage of 2.91% with Sylpot 184 and 1.05% with X-34-4184 at 110 ºC, whereas that of 0.02% or less at 20 ºC or with X-34-4184 at 20 ºC. Sylpot 184 was not fully cured and very soft at 20 ºC curing temperature. Therefore, it was clearly demonstrated that X-34-4184 at 20 ºC can reduce the shrinkage by a factor of 100 or more and indicating that it is an extremely effective material for particularly nanostructure transfer. Temperature rise should be the major factor for thermal shrinkage in varying degrees by the material. These results lead the curing without applying any heat is key for low thermal shrinkage, which was realized by the X-34-4184 in our work.

In summary, the results confirm that the use of a photocurable silicone elastomer in a non-heated process effectively prevents the shape deformation that poses a major problem with existing heat-cured silicone elastomers.

4. Conclusion

In this study, we investigated the use of photocurable silicone elastomer in a non-heated process to obtain increased replication accuracy in fabrication of micro/nanodevices and thereby eliminate the longstanding problem of accuracy reduction by thermal shrinkage with heat-cured silicone elastomers.

We first investigated the optimum light-exposure dose for photocuring and the time response of the curing. The results showed that curing was effectively complete 30 min or less after exposure in a wide range of doses and also that the elastomer remained in a liquid form for several minutes after exposure, which is highly advantageous in applications as a material for mass production by casting and other processes.

When we next investigated the optical and mechanical characteristics properties of the cured elastomer, the results demonstrated that it is superior to existing heat-cured silicone elastomers in optical transmittance extending from the near-IR to the UV regions, and approximately three times as high in tensile strength. Its FTIR spectrum showed that it is essentially the same as existing heat-cured elastomers in structure, and elucidation of the reasons for its higher strength remains for further study.

The accuracy of replication was evaluated, and found that photocured X-34-4184 provided extremely high replication accuracy, which is attributable in large part to its thermal shrinkage of just 0.02%, in marked contrast to the value of 2.91% found for the heat-cured Sylpot 184 silicone elastomer.

In life sciences, which represent one of the major field of application for silicone elastomer devices, as well as the mechanical and optical characteristics investigated in this study, their chemical characteristics are highly important. In this study, the FTIR spectra showed that the molecular structure of X-34-4184 is nearly identical to that of a heat-cured silicone elastomer widely used in this field, and its chemical characteristics may therefore be expected to also be nearly the same.

In summary, the X-34-4184 photocurable silicone elastomer as used in this study clearly surpassed the optical and physical characteristics of materials currently in use, increased the replication accuracy by two orders of magnitude, and demonstrated the effectiveness of photosensitive curing without heating.

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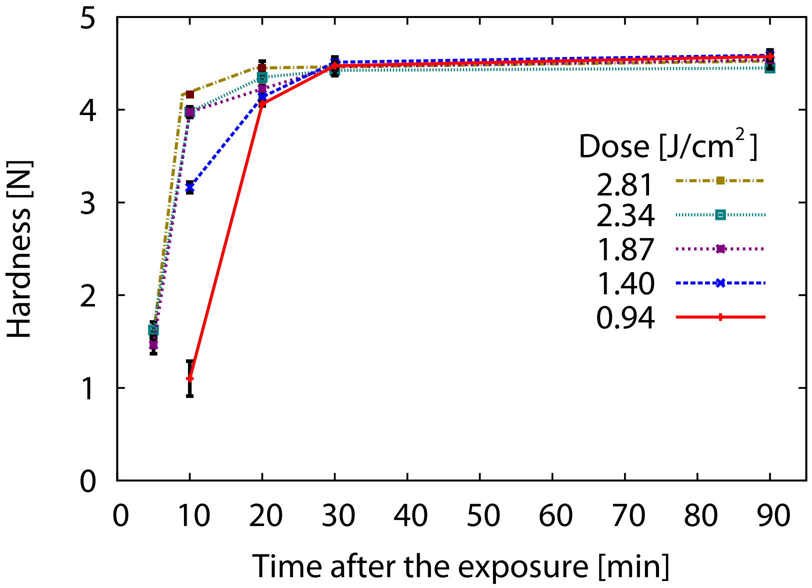

Fig. 1. X-34-4184 curing characteristics. The time course of the post-exposure curing was obtained by measurement of Shore A hardness.

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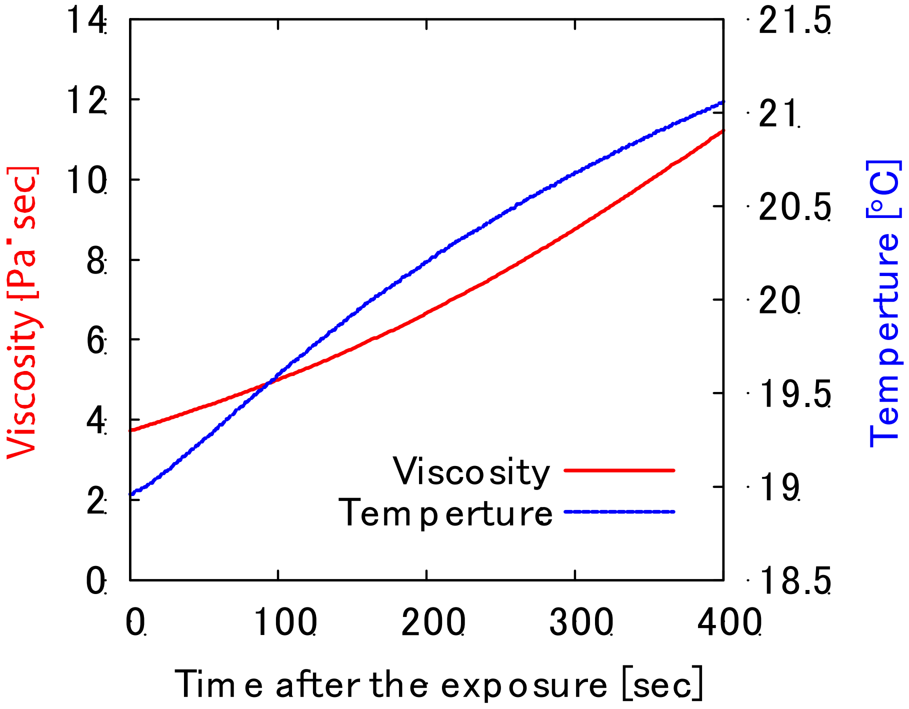


Fig. 2. Changes in viscosity and temperature of the initial post-exposure X-34-4184 in liquid form.

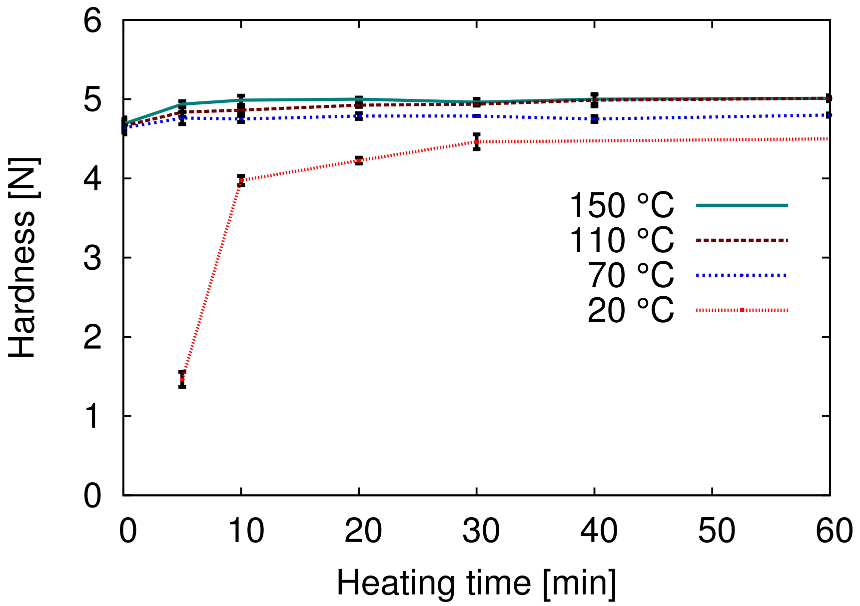


Fig. 3. Temperature dependence of X-34-4184 curing rate.

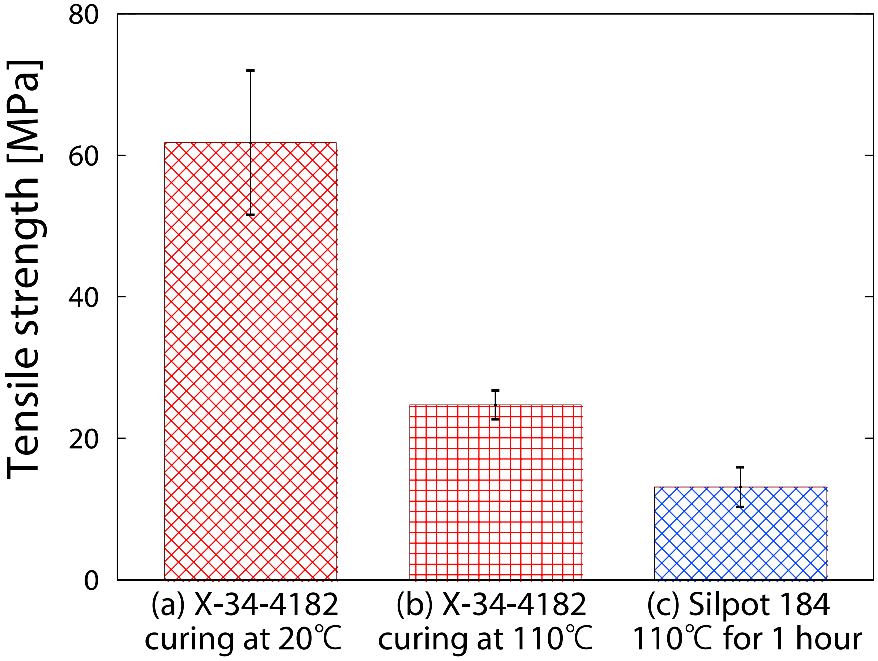


Fig. 4. Dependence of mechanical strength on curing temperature.

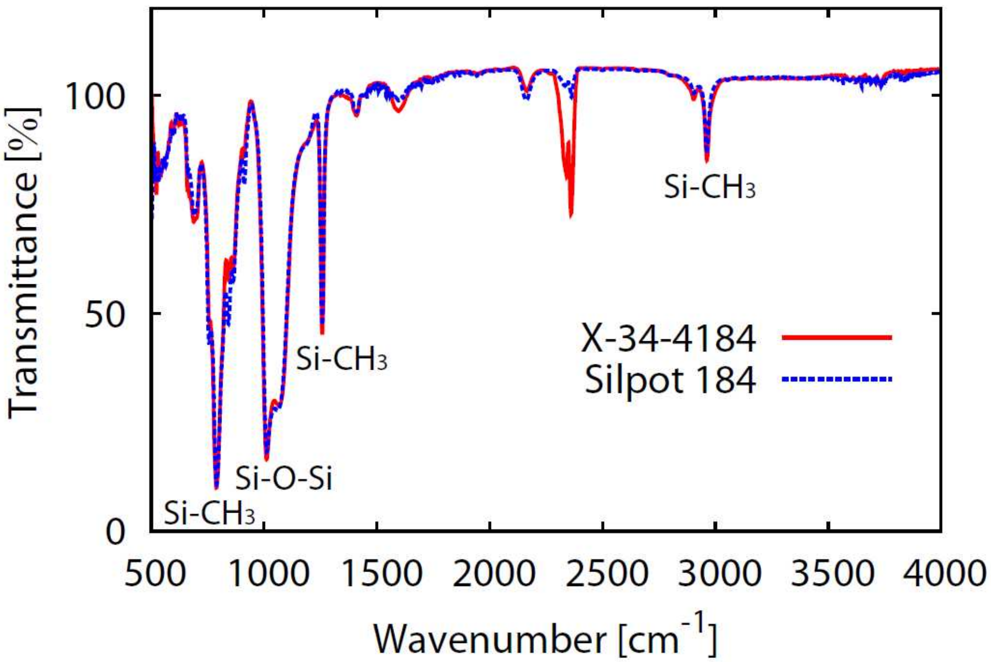


Fig. 5. Comparison of X-34-4184 and Sylpot 184 FTIR spectra. The strong peaks observable between 2280 cm^{-1} and 2400 cm^{-1} for X-34-4184 are presumably attributable to its photocrosslinking agent. The remainder of its spectrum is nearly identical to that of Sylpot 184, thus indicating that Sylpot 184 and X-34-4184 are nearly identical in basic molecular structure.

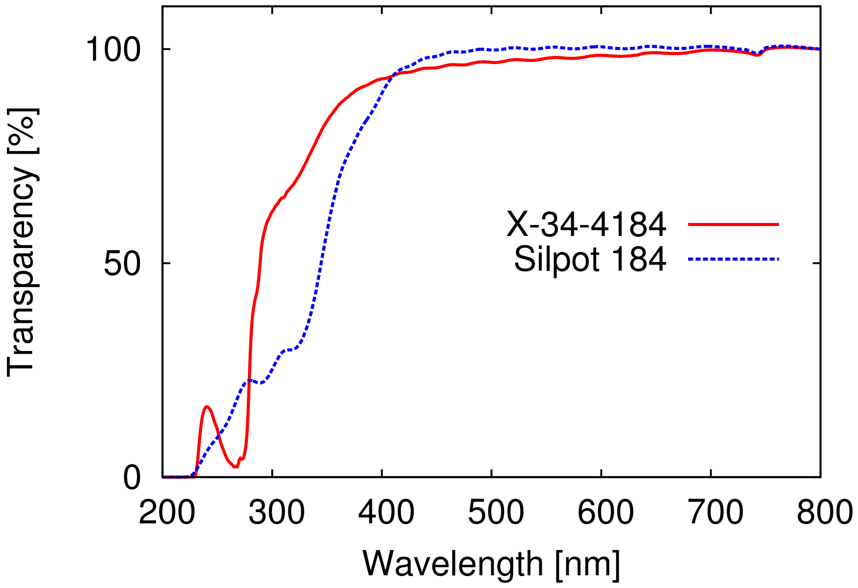


Fig. 6. Comparison of Sylpot 184 and X-34-4184 light transparency characteristics. The X-34-4184 absorption peaks around 250 nm are presumably attributable to its photocrosslinking agent. The remainder of its spectrum is nearly identical to that of Sylpot 184, thus indicating that it will exhibit nearly the same physical properties.

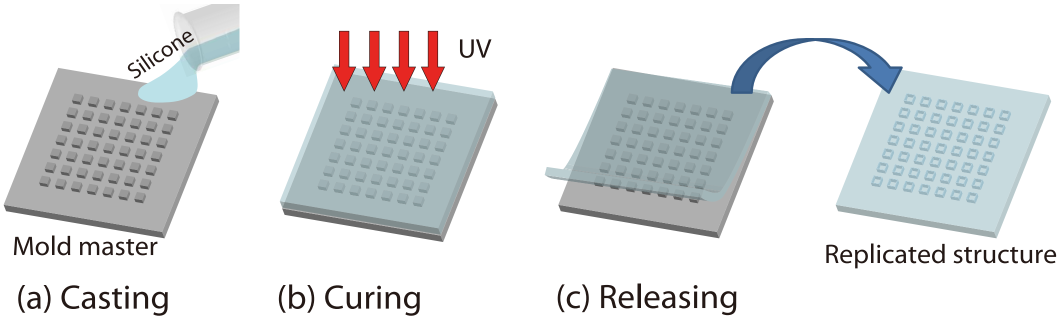
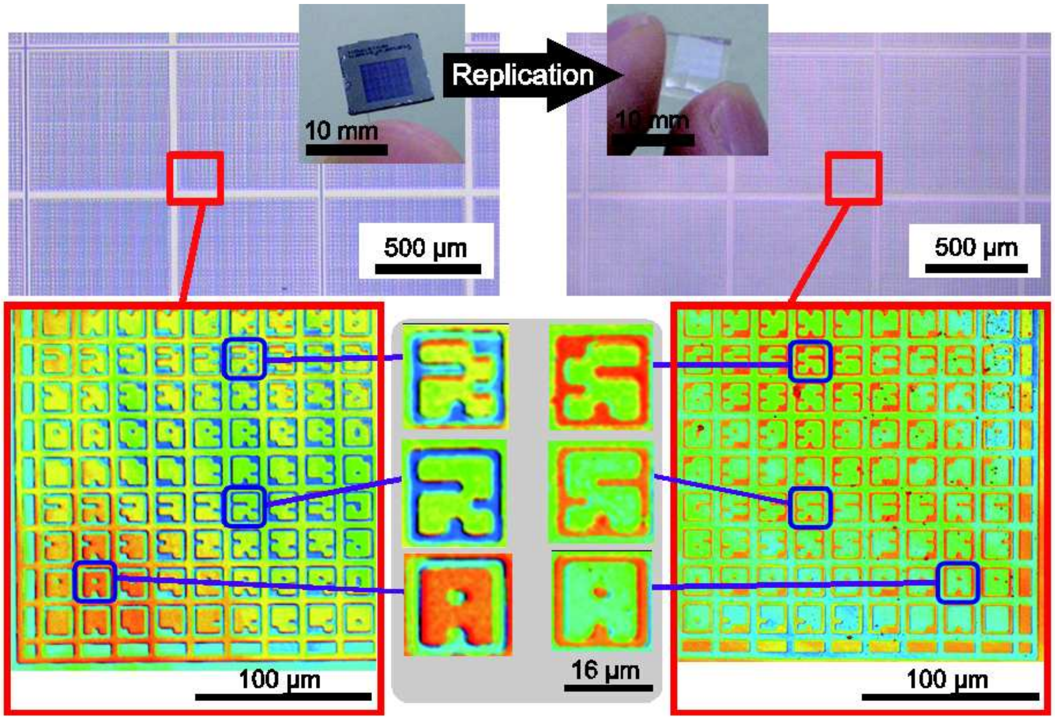


Fig. 7. Photocurable silicone elastomer replication procedure: (a) pouring the non-polymerized elastomer onto the mold, (b) exposure, and (c) peeling off.



(A) Mold master

(B) X-34-4184

Fig. 8. Typical microstructure replication: (A) Si mold with engraved microstructure pattern, and (B) photocured silicone elastomer microstructure obtained by transfer from the master. As shown, the mold pattern is reversed in the replication process.

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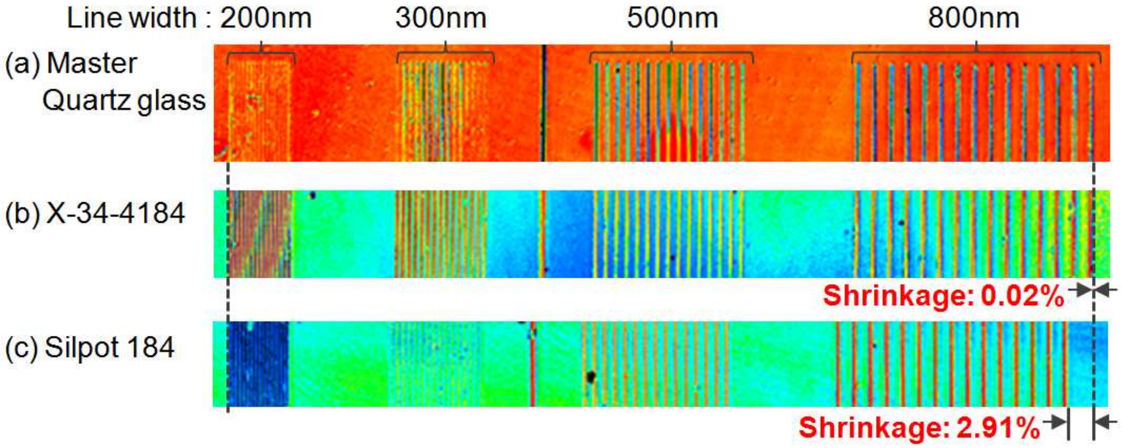

Fig. 9. Results of transfer of nanoscale line-and-space fine structure. The line groups each contain 15 lines, in line widths of 200, 300, 500, and 800 nm, all with a line:space ratio of 1:3. (a) Mold master, (b) X-34-4184, and (c) Sylpot 184.

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