Dimensional stability analysis of a UV printed polymer microstructure for a novel glazing system

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Abstract

The dimensional stability of a UV printed polymer microstructure for a novel glazing system for seasonal regulation and daylighting based on a periodic array of parabolic micro-mirrors is investigated. The objectives of the work are: i) to analyze the dimensional changes of UV-printed microstructures related to polymerization and thermal aging; and ii) to identify the impact of these changes on the optical properties of the system. The period was found to be stable, with shrinkage below 1.5% after printing, independent of PI concentration, and remained constant upon thermal exposure. In contrast, dimension $W_{1/2}$ decreased by up to 14.5% with time at 80°C, presumably due to physical aging processes. A change of height also occurred, but it was partly compensated by the change of $W_{1/2}$ as a result of Poisson's effects and a complex distribution of internal stress. The impacts of these dimensional changes on the redirection of daylight were also investigated.

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1. Introduction

Highly glazed buildings have become a worldwide design trend in modern architecture. However, glazing may induce large thermal loss in winter while increasing cooling load in summer, and it may also cause glare and visual discomfort due to non-uniform light distribution within an interior space. A multifunctional complex fenestration system with embedded light-redirecting micro-mirrors has been developed [1]. As shown in Fig. 1 (a) [2], this system consists of a one-dimensional array of parabolic reflective surfaces coupled with an array of secondary reflective surfaces. In winter the incoming solar radiation is redirected by the reflective parabolic surface to reach the rear of a room. In contrast, in summer where the elevation angle is high, the direct solar radiation is focused on secondary reflective surfaces and reflected outside. Through this method, seasonal thermal control is realized. Thanks to the micrometric size of the embedded mirrors, clear view without obstruction through the system is achieved, as shown in Fig. 1 (b). The preparation of embedded micro-mirrors requires the fabrication and replication of transparent polymer microstructures, as well as the deposition of a reflective material on the microstructures. Polymerization shrinkage and further time-dependent structural relaxation and associated distortion of the shape of such microstructures may occur, and thus the optical performance of the glazing system may change over time.

The present work focuses on i) analyzing the dimensional changes of UV-printed microstructures related to polymerization and thermal aging; and ii) identifying the impact of these changes on the optical properties with respect to redirection of the system. An acrylated hyperbranched polymer (HBP) was selected owing to its intrinsically low shrinkage [3,4,5], and attention was paid to the amount of photoinitiator (PI) and accelerated aging at 80°C (with acceleration factor of approximately 30 with respect to aging at 20°C) for up to three weeks on the dimensions of the printed microstructures. Unaged and aged microstructures were carefully cut and characterized using an optical microscope. The impacts of dimensional changes on the redirection of daylight were investigated.

![Fig.1. Basic principle of the glazing with micro-mirrors: (a) model of embedded micro-mirrors in a polymer layer for ray-tracing simulation; (b) View of the logo of École polytechnique fédérale de Lausanne (EPFL) through the conventional glass and the glass with the polymer layer which consists of embedded micro-mirrors.](image)

2. Methods

A master mold with the desired microstructure was fabricated by excimer laser ablation. The wavelength of the laser is 248 nm. The height of the microstructure of the master mold is 93 ± 1 μm and the periodicity is about 50 ± 0.2 μm. The structured area was 2 cm × 2 cm. A two-step replication process was used to transfer the microstructures on a glass substrate. First, a template with negative microstructures with respect to the master mold was prepared by casting polydimethylsiloxane (PDMS) in the master mold. 22 g of PDMS was poured on the master mold and degassed under a vacuum chamber for about 40 min. Second, the original positive microstructures were replicated from the PDMS negative template by UV-cured acrylated hyperbranched polymer (HBP) on a 7.4 cm x 2.5 cm glass substrate. A hyper-branched acrylate polymer (HBP, CN2302 Sartomer) was mixed with a trimethylbenzoyl phosphine oxide photoinitiator (PI, TPO, ESACURE) with an activation wavelength between 360
nm and 420 nm. In the present work, three different concentrations of PI were prepared: 1.5 wt %, 3 wt %, and 6 wt %. After the acrylated HBP homogeneously flowed through the structure, the sample was exposed to UV light at an intensity of around 8 mW/cm² with the emitted wavelength of 375 nm for 180 s. After that, the sample was flipped and exposed to the same intensity for 90 s, in order to ensure homogeneous photo-conversion of the 180 ± 20 μm thick sample, and finally manually detached from the PDMS template. Samples for each concentration of PI are prepared at room temperature. The samples prepared with 6 wt% of PI were further aged in an oven at 80°C for 1 week, 2 weeks and 3 weeks. It was assumed that at this temperature the aging rate related to dimensional changes was increased by a factor of approximately 30 with respect to that at 20°C [6], so that 3 weeks corresponded to approximately 8 years at 20°C. Cross-sections of the printed microstructures and PDMS negative template were carefully cut by scribing the backside of the samples with a razor blade and manual fracture and were observed under an optical microscope (Olympus BX60). The height (H), periodicity (P), and width at mid-height (W₁/₂) of the microstructure shown in Fig. 2 were measured with 1 μm accuracy. The parabolic surface where a highly reflective material (a mirror) is deposited is indicated with a red curve and the height of the mirror is the full height H minus 5 μm (H-5), as shown in Fig.2.

Four tips for each concentration of PI were selected and their contours were extracted using the software WebPlotDigitizer with step size around 2.5 μm. The contour of the negative PDMS microstructure was also determined as a reference. The parabolic edge of individual tips was fitted with second order polynomial functions. The relative changes of dimensions of H, P, and W₁/₂ with respect to the PDMS reference were calculated. The extracted parabolic edges were used for ray-tracing simulation with CFSpro [7] and their angular dependent transmittances at normal incidence were calculated, in order to analyze the impacts of the dimensional changes on the redirection of daylight.

![Fig. 2. An example of the UV-cured polymer microstructure and the indication of the measured parameters.](image)

### 3. Results and discussion

Polymerization shrinkage in UV-cured polymers is the result of a change in the intermolecular distances of the monomers from initial van der Waals length scales to the covalent bond lengths during photo polymerization. The volumetric shrinkage-strain is approximately proportional to the degree of conversion of the monomer systems at least up to the vitrification point [8]. Generally speaking, a higher concentration of PI may result in higher conversion, i.e., higher polymerization shrinkage. However, due to the complex distribution of internal stresses in the high-aspect ratio structure with a sharp tip and the Poisson’s effect, the dimensional changes in different directions (e.g., H and W₁/₂) may not be a simple function of the degree of conversion. The Poisson effect [9] is the phenomenon in which a material tends to expand in directions perpendicular to the direction of compression. Conversely, if the material is stretched rather than compressed, it usually tends to contract in the directions transverse to the direction of stretching.
Fig. 3 shows the dimensional changes of the UV printed HBP microstructure. The data represent the normalized shrinkage in absolute values, $\Delta x/x_0$, where $\Delta x = |x - x_0|$ and $x$ and $x_0$ are one of the dimensions (P, H and $W_{1/2}$) of the molded HBP and the reference PDMS, respectively. The periodicity $P$ was found to slightly contract and remained within 1.5% equal to that of the PDMS template. This result was consistent with the fact that in-plane shrinkage was restricted in the periodic microstructure due to lateral confinement during UV polymerization, and the resulting tensile stress only partly relaxed upon demolding in the solid state. The shrinkage of the height $H$ was about 11% on average for the case with 1.5% PI. It decreased to 3% for 3% PI, and increased to 5% for 6% PI. The trend for $W_{1/2}$ was the opposite, going through a maximum shrinkage close to 10% at 3% PI, so that the product of shrinkage along the height and width was independent of PI concentration within experimental scatter. This result indicates that the Poisson effect indeed contributed to the anisotropy in dimensional changes. Such rather complex behavior reveal the intricate interplay between polymerization shrinkage and associated stress build up, and viscoelastic relaxation processes as already reported for UV printed polymer gratings [10].

Fig. 4 shows the dimensional changes measured at ambient temperature as a function of exposure time under accelerated aging at 80°C for a printed HBP microstructure with a concentration of 6% of PI. The periodicity $P$ progressively decreased with time (i.e. shrinkage increased). In this case the microstructure was not confined in plane, in contrast with the process-induced shrinkage shown in Fig. 3. The observed evolution might be due to both chemical aging and physical aging. The photo-induced conversion of the acrylated HBP may indeed proceed as a thermally activated rate process, leading to additional shrinkage. Further thermally activated processes such as thermo-oxidative and hydrolytic degradation cannot be excluded, but should be marginal at the investigated temperature. One may also invoke physical aging, which occurs when a polymer is cooled below its glass transition temperature $T_g$, and evolves toward thermodynamic equilibrium. This evolution is characterized by the slow decrease of the free volume and enthalpy of the polymer. The dimension $W_{1/2}$ also increased with aging time, up to 14.5%, and, again, followed an opposite trend to the change of height $H$. It should be noted that the microstructure will be constrained when encapsulated with another polymer counterpart in the glazing system, i.e., the dimensional changes should be less severe under aging.

The impacts of these dimensional changes on the redirection of daylight are presented in Fig. 5 for the three investigated concentrations of PI. Fig. 5 (a) shows the actual shapes of the micro-mirrors and corresponding quadratic fits. Fig. 5 (b) shows an example of modeling for ray-tracing simulations. The refractive indexes of glass and the used polymer were the same (refractive index $n = 1.5$), and therefore, the glass pane where the polymer layer was attached, was not modeled in the present simulation for the convenience of viewing. Plots of the total transmittance and transmittance of redirected rays are presented in Fig. 5 (c). The total transmittance (namely $T_{tot}$) is the sum of redirected rays ($T_{up}$) and direct-transmitted rays. The transmittance of redirected rays reaches a maximum value when it becomes equal to the total transmittance, i.e., when redirection for all rays at a given angle occurs on the micro-mirrors. The corresponding incident angle $\alpha$ defined in Fig. 5 (b) is:

Fig. 3. Dimensional changes with the variation of the concentration of the photoinitiator.

Fig. 4. Dimensional changes as functions of exposure time under accelerated aging at 80°C.
where $y_{n-1}$ is the value of $y$ as a function of a secondary polynomial fit for the $n$-1 mirror (Fig. (a)), and the unit for the variables and the constants is μm. Therefore $\alpha$ is the angle between the line defined by the starting point of the $n^{th}$ mirror and the end point of the previous ((n-1)$^{th}$) mirror, and the horizon through the end point at the (n-1)$^{th}$ mirror.

\[
\alpha = \tan^{-1}\left(\frac{(y_{n-1} + 50)}{(H - 5)}\right)
\]  

Fig. 5.: (a) extracted micro-mirrors profiles (points) and corresponding quadratic fits; (b) ray-tracing analysis of model parabolic micro-mirrors embedded in a polymer layer with refractive index of 1.495 showing direct-transmitted rays and reflected rays; (c) total transmittance ($T_{tot}$) and transmittance of redirection ($T_{up}$) as a function of incident angle at normal incidence; (d) derivatives of the polynomial fits as functions of the height of parabolic surfaces.

The angles $\alpha$ calculated are 33° (PDMS), 39° (1.5% PI), 34° (3% PI) and 37° (6% PI), after conversion with respect to the refractive index based on the Snell’s law [11], corresponding to the incoming angles 55°, 70°, 57°, 63° in Fig. 5 (c). Comparison of the cases for 1.5% PI and 6% PI shows that the change of the incoming angles of maximum redirected transmittance is significantly affected by the dimensional change in H but not sensitive to the dimensional change in $W_{1/2}$. When the incident angle is larger than 70°, for the four cases the transmittance is only contributed from redirected rays. The transmittances for 1.5% PI and 6% PI are approximately identical in the angular range between 70° and 90°, while for the cases of the PDMS and 3% PI case, the transmittances are relatively lower. The difference of the transmittance in the angular range between 70° and 90° results from the different average slopes. Fig.5 (d) shows the derivative (e.g. the slope) of the fitted curves as a function of micro-mirror height H from Fig. 5 (a). The angle of incoming rays at the interface 2 between the back side of the polymer and air will change after being redirected by the parabolic mirrors. For the incident angle of 70°, the average slopes
over the parabolic segment covered by the incoming rays for the four cases are -0.046 (PDMS), -0.09 (1.5% PI), -0.054 (3% PI) and -0.108 (6% PI), respectively. In the present coordinate system, a negative slope implies a decrease of incoming angles for the interface 2 and thus contributes to the increase of transmittance, while a positive slope has the opposite effect. Since reflection on interface 1 increases with the increase of incident angle, it is expected that the maximum redirected transmittance at 57˚ for the case of 3% PI was larger than that for the case of 6% where maximum redirected transmittance is at 63˚; however, it is the other way around, as slopes which are larger than 0.079 (marked in Fig. 5(d)) will result in total reflection on interface 2, and thus considerable reduction of transmittance may occur.

4. Conclusions

The dimensional stability of a UV printed periodic polymer microstructure for a novel glazing system, produced with different concentrations of PI and under thermal aging was investigated. The period was found to be stable, with shrinkage below 1.5% after printing, independent of PI concentration, and which remained rather constant upon thermal exposure. In contrast, dimension \( W_{1/2} \) decreased by up to 14.5% with time at 80°C, presumably due to additional chemical conversion and physical aging processes. A change of height also occurred, but it was partly compensated by the change of \( W_{1/2} \) as a result of Poisson's effects and a complex distribution of internal stress. The impacts of dimensional changes on the redirection of daylight were also investigated. The dominant reason accounting for the change of the angular dependence and intensity of the maximum transmittance of redirected rays was the shrinkage of the micro-mirrors along their height \( H \) and resulting change of their local curvature.

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