Fabrication of Flexible Polymer Molds for Polymer Microstructuring by Roll-to-Roll Hot Embossing

Nischay Kodihalli Shivaprakash,* Thomas Ferraguto, Artee Panwar, Shib Shankar Banerjee, Carol Forance Barry,* and Joey Mead*†

Nanomanufacturing Center, Department of Plastics Engineering, University of Massachusetts Lowell, 1 University Avenue, Lowell, Massachusetts 01854, United States

ABSTRACT: Roll-to-roll hot embossing could revolutionize the manufacturing of multifunctional polymer films with the ability to process large area at a high rate with reduced cost. The continuous hot embossing of the films, however, has been hindered due to the lack of durable and flexible molds, which can replicate micro and nanostructures with reliability over several embossing cycles. In this work, we demonstrate for the first time the fabrication of a flexible polymer (polyimide) mold from the commercially available sheet by a maskless photolithography approach combined with inductively coupled plasma etching and its potential application to the roll-to-roll hot embossing process. The flexible polyimide mold consisted of holes with controlled dimensions: diameter: 14 μm, spacing: 16.5 μm, and depth: 6.8 μm. The reliability of flexible polyimide mold was tested and implemented by embossing micron-sized features on a commercial thermoplastic polymer, polyamide, and thermoplastic elastomer (TPE) sheet. The polyimide mold replicated micron-sized features on polymer substrates (polyamide and TPE) with excellent fidelity and was durable even after numerous embossing cycles.

1. INTRODUCTION

Large-area structuring of polymer surfaces with micro- and/or nanostructures has widespread applications in areas of self-cleaning surfaces, sensors,1 biodevices,2 flexible displays,3 waveguides,4 and MEMs devices.5 A high demand exists in the manufacturing of such surface structures at low cost and improved productivity. To address this challenge, static hot embossing (SHE)6 and nanoimprint lithography (NIL)7 processes were introduced for micro-/nanostructuring in polymers.

In a typical SHE process, a thermoplastic polymer sheet is heated above the glass transition temperature (Tg) and imprinted by a mold containing the micro-/nanostructures. Due to the applied temperature and pressure, the softened polymer sheet undergoes mold filling; subsequently, the embossed polymer sheet with micro-/nanostructures is cooled below the Tg before demolding. Molds are a critical part of the micro/nanostructuring process. Since the process involves softening a polymer sheet beyond Tg and application of high pressure (16 MPa), the molds must possess sufficient strength to survive such extreme environments and also last for many runs. The SHE process employs planar molds typically made from electroplating of nickel over a master template fabricated either by photolithography8 or e-beam lithography9 (depending on the feature size), epoxy,10 and deep reactive ion etching11 or potassium hydroxide wet etching in silicon.12 Silicon wafers, being extremely fragile, are somewhat limited in their widespread acceptance as a mold material in SHE processes, and often nickel is used as a mold.13

In contrast to the SHE process, the NIL process consists of two variants depending on the type of polymer and its associated curing mechanism: thermal NIL (hot embossing) and ultraviolet NIL (UV-NIL).13 In thermal NIL, a thermoplastic polymer resist is heated above the glass transition temperature (Tg) and imprinted by a mold containing nanostructures/patterns. Under the influence of temperature, pressure (typically about 0.3–10 MPa), and time, the polymer resist undergoes mold filling, allowing complete replication of nanostructures. In the next stage, the polymer resist is cooled below the Tg to attain necessary stiffness before they are separated from the mold. Similar processing steps exist in the case of UV-NIL, but the surface structuring is performed with a UV-curable resist. The resist is coated over a transparent polymer substrate and undergoes hardening by UV irradiation. Since the imprinting is done at room temperature using a liquid resist, less pressure (~0.3 MPa) is needed to force the polymer into the cavities during imprinting. Thus, the requirements for the mold material in terms of strength and thermal stability are insignificant compared to the SHE process.13

Received: May 20, 2019
Accepted: June 25, 2019
Published: July 22, 2019
For the UV-NIL process, UV-transparent molds are made from poly(dimethylsiloxane) (PDMS), polyurethane acrylate, poly(vinyl chloride), quartz and organic–inorganic hybrid resin. The flexible molds are either cast or thermally imprinted from a master template (silicon and quartz) containing nanostructures fabricated via traditional e-beam or deep UV lithography and reactive ion etching. PDMS molds, however, do not possess sufficient elastic modulus to withstand the pressure and temperature encountered in the thermal NIL process. Due to its low elastic modulus, PDMS molds are not preferred to replicate high density sub-100 nm resolution features limiting their widespread acceptance as a mold material. Electroformed nickel, perfluoropolyether (PFPE), and acrylate are commonly used as mold materials in the thermal NIL process due to their high modulus (1.6 GPa for PFPE) and excellent release properties arising from their low surface energy (e.g., PFPE). Additionally, PFPE can become soft above a certain temperature, which enables easy replication from an original silicon or quartz master template via the thermal NIL process. Nevertheless, the two processes, SHE and NIL, suffer in terms of productivity as they are batch processes and have long cycle times (around 30 min).

Alternative continuous processing methodologies such as roll-to-roll nanoimprint lithography (R2R-NIL, both thermal and UV), roll-to-roll extrusion coating (R2R-EC), and roll-to-roll hot embossing (R2R-HE) were introduced to improve the productivity for surface structuring over large areas. The mold material used for roll-to-roll processes and have long cycle times (around 30 min).

Alternative continuous processing methodologies such as roll-to-roll nanoimprint lithography (R2R-NIL, both thermal and UV), roll-to-roll extrusion coating (R2R-EC), and roll-to-roll hot embossing (R2R-HE) were introduced to improve the productivity for surface structuring over large areas. The mold material used for roll-to-roll processes and have long cycle times (around 30 min).

Seamless roller molds are fabricated either by curved surface lithography or direct laser interference patterning (DLIP). Curved surface lithography using UV, e-beam, or X-ray follows similar steps as in the conventional lithography process. The only difference is that patterning, exposure, chemical development, etching, and electropolishing are all performed on a curved roller surface using appropriate photoresists. Striegel et al. successfully demonstrated the fabrication of a continuous nickel sleeve via curved surface UV lithography, which allowed the replication of circumferential channel or groove-like structures with a depth of 5 μm by R2R-HE on a variety of substrates, including polypropylene, poly(tetrafluoroethylene), polyetherketone, polyethersulfone, polysulfone, aluminum, and copper. Seamless mold fabrication by DLIP offers several advantages such as high-resolution patterning and fast operation, as it relies on the generation of the interference pattern by overlapping two or more laser beams over the substrate surface. Corresponding to the locations of interference maxima, the substrate surface can be ablated either by photothermal or photochemical routes. Rank et al. employed the DLIP method in combination with a picosecond laser source to structure nickel sleeves with periodic line-like microstructures having spatial periods between 1.5 and 5 μm. The resulting nickel sleeves were then used for R2R-HE of a poly(ethylene terephthalate) (PET) film at web speeds ranging from 2 to 50 m/min. Several limitations exist for both curved surface lithography and DLIP fabrication techniques. The former method utilizes expensive masks whose fabrication is not trivial as it is laborious, requires a sophisticated rotation stage equipped with a high-precision step motor adding to complexity and manufacturing costs. The latter technique has shortcomings with regards to the feature size and geometry (i.e., only periodic sinusoidal structures can be made using DLIP).

Considerable attention has been given to the use of polyimide as polymeric molds in UV-NIL, static hot embossing (thermal NIL), and microinjection molding processes due to their inherent flexibility, similar coefficient of thermal expansion with the polymer substrate used for imprinting, high glass transition temperature ($T_g$), exceptional thermal stability and good mechanical and chemical properties. Wu et al. fabricated flexible polyimide molds (P11, P12, and P13) by casting synthesized polyimide solutions with (P12 and P13) and without (P11) fluorine groups on a silicon master template. Thermal NIL was performed using the P11 mold on a poly(methyl methacrylate) (PMMA) liquid resist coated
over a transparent PET substrate. The UV-NIL process was conducted using molds P12 and P13 on a UV-curable photoresist coated over a PET substrate. Successful transfer and demolding of micro- (19 μm) and nanostructures (140 nm) were observed for P12 and P13 molds without requiring a low surface energy release layer due to the presence of fluorine groups on the backbone chain, an additional low surface energy treatment, however, was applied to the P11 mold for easy release. The viscosity of PMMA liquid resist was extremely low, and only 0.02 MPa pressure was applied during the thermal imprinting process. Prior work by Kim et al. 40 investigated the use of polyimide—chromium hybrid tooling under high temperature, high shear, and high-pressure environments of the injection molding process. The results showed better replication of microfeatures at lower mold and melt temperature with polyimide tooling compared to the polymer-backed silicon molds, and this was attributed to the longer solidification times caused due to the delayed heat transfer by the polyimide hybrid molds.

In this study, we report the use of a flexible polyimide mold in the R2R-HE process, which was fabricated by a maskless photolithography approach using a commercially available polyimide sheet. The proposed mold fabrication methodology eliminates the need for complex electroplating steps, thus allowing an easier route to produce flexible polymeric molds for the R2R-HE process. This approach is particularly advantageous for preliminary studies and prototyping as it enables quick and low-cost fabrication of the molds. To satisfy the requirements of high mechanical strength (modulus) and flexibility, a detailed evaluation of the mold material with respect to mechanical, thermal, and dynamic mechanical properties was performed and compared with polymer substrates used for the imprinting process. Finally, the reliability of the flexible polyimide mold was evaluated by embossing microfeatures on polyamide and thermoplastic elastomer (TPE) sheet.

2. EXPERIMENTAL SECTION

2.1. Fabrication of Flexible Polyimide Mold. The flexible polymer mold was fabricated on a commercially available polyimide sheet (thickness: 140 μm) (Kapton B, Dupont, Wilmington, DE) (please note that this PI sheet is UV transparent). The roughness of the polymer sheet was critical for this process. Several other PI sheets were too rough for this application.

The preliminary investigation was performed to fabricate flexible polyimide mold with the lift-off and dry etching processes using the titanium as a metal mask. The lift-off and dry etching fabrication procedures produced microstructures with poor dimensional control. In addition, flexible polyimide mold fabricated via the dry etching method was only useful to produce shallow microstructures with a very low aspect ratio (height/diameter = 0.1:1) due to poor etch selectivity between the titanium metal mask and the polyimide layer. To overcome these shortcomings, an alternative robust fabrication route as outlined below was employed.

First, a 1000-Å-thick layer of nickel was deposited on the polyimide substrate using e-beam evaporation. The processing parameters for nickel deposition are listed in Table 1. In the next step, a photoresist (Shipley, Microposit S1813, Newton, MA) was spin-coated on the nickel-coated polyimide using a speed of 2000 rpm and time of 60 s and then was soft-baked at 115 °C for 60 s. Features with desired diameter and spacing were created in the photoresist with the Direct Write system (Heidelberg Instruments, Heidelberg, Germany). The features then were developed for 40–60 s using a commercial developer (Megaposit MF-26A, Dow Electronic Materials, Marlborough, MA), which removed photoresist from the holes and exposed the nickel. The photoresist was hard-baked at 180 °C for 6 min. After hard baking of the photoresist, nickel was selectively removed from the holes using a chemical etchant (i.e., nickel protected by the photoresist was not etched). Then, the hard-baked photoresist was removed using acetone and isopropyl. With the nickel mask left, the polyimide was dry-etched using an inductively coupled plasma etching technique. The detailed schematic representation of the fabrication methodology is outlined in Figure 1.

2.2. Roll-to-Roll Hot Embossing of Trapezoidal Structures. Two polymeric materials were used to evaluate the fabricated polyimide mold in the R2R-HE process. First, a 200-μm-thick thermoplastic elastomer (TPE) sheet based on the acrylic block co-polymer was obtained from Kuraray Co. Ltd. (grade: Kurarity) and, second, a microcrystalline polyamide was extruded into 300-μm-thick sheet. The microcrystalline polyamide pellets (Trogamid CX7323) purchased from Evonik-Industries were extruded using a twin-screw extruder (TECHNOVEL Corporation, Osaka, Japan, model KZW 15TW) and a sheet die with a coat hanger manifold. The polyamide’s low melt strength required a film extrusion configuration in which the die feds melt downward onto the chill rolls. Prior to extrusion, polymer pellets were dried at 95 °C for 8 h. Lower-than-recommended barrel and die temperatures (232–252 °C) prevented degradation during extrusion, and high chill roll temperatures (140 °C) mandated oil heating of the chill rolls. These parameters enabled the extrusion of 150-mm-wide polyamide sheet.

For hot embossing, the flexible polyimide mold with the 14-μm-diameter holes was mounted on a steel roller. During the mounting procedure, the fabricated polyimide mold was bonded onto a polyimide belt using a high-temperature epoxy adhesive. Then, the flexible polyimide mold and belt assembly were wrapped around the roller by placing it firmly inside a machined slot using bolts and steel plates (as shown in Figure 2, top section). For embossing, the polyamide and TPE sheets were held between two rollers. The rolls softened the sheet; it was not preheated. On the application of suitable nip pressure and roll speed, the softened polymer was forced into the microcavities of flexible polyimide mold. A graphical representation of the roll-to-roll hot embossing process is illustrated in Figure 2 (bottom). The robustness of fabricated polyimide mold for embossing was evaluated by varying the mold temperatures ($T_{\text{polyamide}}$), whereas the nip pressure ($P_{\text{nip}}$) and roll speed ($V_{\text{R}}$) were kept constant. The process parameters are listed in Table 2.

2.3. Characterization. 2.3.1. Dynamic Mechanical Analysis (DMA). DMA of the unstructured polyimide, polyamide, and TPE sheet was carried out in tensile mode using the TA Instrument machine (DMA Q800). Temperature parameters are listed in

| Table 1. Process Parameters Used for Nickel Deposition Using e-Beam Evaporation |
|---------------------------------|-------|
| target metal                   | nickel|
| deposition rate                | 2 Å/s |
| base pressure                  | 5 × 10⁻⁶ Torr |
| temperature                    | 25 °C  |



ACS Omega 2015, 4, 12480−12488
sweeps tests were performed over a temperature range of −150 to 200 °C at a heating rate of 2 °C/min, a frequency of 1 Hz, and a strain amplitude of 30 μm. The storage modulus ($E'$), loss modulus ($E''$), and loss tangent ($\tan \delta = E''/E'$) were measured and analyzed as a function of temperature.

2.3.2. Thermogravimetric Analysis. The thermal stability of the unstructured polyimide, polyamide, and TPE sheet was determined using thermogravimetric analysis (TGA). A TA Instruments (model: Q50) with a heating rate of 20 °C/min and a temperature range from 20 to 800 °C in nitrogen atmosphere was used for these measurements.

2.3.3. Field Emission Scanning Electron Microscopy (FESEM). Field emission scanning electron microscopy (FESEM, Joel, model: JSM-7401F) was used to record the trapezoidal structures fabricated on the polyamide surface. FESEM measurements were conducted at an acceleration...
Table 2. Process Parameters Used To Evaluate Flexible Polyimide Mold by R2R-HE

| polymer sheet | $T_{polyimide} \, (^{\circ}C)$ | $P_{trap} \, (MPa)$ | $V_{s} \, (m/min)$ |
|---------------|-----------------|-----------------|-----------------|
| polyamide     | 140             | 3.7             | 0.1             |
|               | 145             |                 |                 |
|               | 150             |                 |                 |
| TPE           | 90              | 3.7             | 0.1             |
|               | 95              |                 |                 |
|               | 100             |                 |                 |

voltage of 10.0 kV. The sample surfaces were gold-coated to avoid charging on exposure to electron beam during the measurements.

3. RESULTS AND DISCUSSION

3.1. Fabrication and Thermomechanical Characterization of Flexible Polyimide Mold. The optical microscopy images of the polyimide mold (fabricated as outlined in Figure 1) during various stages of fabrication, post chemical development, after wet etching of exposed nickel layer, and after dry etching, are shown in Figure 3a−c, respectively. The resulting tooling after the dry etching step had holes with consistent diameters of 14 μm, spacings of 16.5 μm, and depths of 6.8 μm; the accuracy of these dimensions was validated using FESEM image (Figure 3d) and surface profilometry (not shown here). The measured feature dimensions were comparable to those reported in the literature with a special exclusion to the features in nanometer length scale fabricated via casting route, as demonstrated previously by Wu and co-workers. The smallest feature dimensions that can be fabricated using the methodology (outlined in Figure 1) were dependent on the laser diode wavelength used in the Direct Write system (Heidelberg Instruments, Heidelberg, Germany) and the surface roughness of unstructured polyimide sheet.

The efficient demolding of microfeatures is important to maintain the fidelity of the embossed features. To reduce adhesion forces between the tooling and polymer sheet, a deposition of a PFTS antistiction layer displayed a contact angle of 117° (Figure 4b) for water, indicating a hydrophobic, low surface energy substrate, expected to assist in demolding of the embossed microfeatures.

For the R2R-HE process, a mold must possess the flexibility to be wrapped around the roller, high mechanical strength (modulus) at processing temperature to withstand high nip pressure, thermal stability to prevent degradation at processing temperature, and durability for repeated use. A flexible mold can provide a larger conformal contact with the substrate, thereby reducing the pressure required during the embossing step. Additionally, a flexible mold enables easy demolding of embossed microfeatures due to a smaller demolding area relative to a rigid mold. It is also reported that the $T_{g}$ of the polymer material being used as a flexible mold is considered critical for performance, and the mold material should have a higher $T_{g}$ compared to the polymers that will be embossed to avoid tooling damage. Thus, it is necessary to evaluate the mechanical and thermal performance of the mold substrate for successful implementation in the roll-to-roll hot embossing process.

The storage modulus ($E’$), loss modulus ($E''$), and loss tangent (tan δ = $E''/E’$) of the unstructured polyimide, polyamide, and TPE were measured as a function of temperature (Figure 5a−c). From the tan δ and $E''$ curves of the TPE sheet, two peaks at about −45 and 105 °C were due to the glass transition temperature ($T_{g}$) of the poly(butyl acrylate) soft segment and poly(methyl methacrylate) hard segment, respectively. Similarly, for the polyamide, two transition peaks appeared at about −60 and 128 °C. The transition peak at −60 °C was considered an indication of the $\beta$ transition from the formation of hydrogen bonds between the carbonyl group of polyamide and absorbed water molecules. A narrow and tall tan δ peak at 128 °C ($\alpha$ transition: $T_{g}$) was due to the amorphous regions (Figure 5c). There was a slight increase in the modulus value of polyamide at temperatures beyond 150 °C because of the cold crystallization phenomenon, as reported elsewhere. The $E’$ values for the polyamide were fairly high across the tested temperature range, whereas $E’$ decreased rapidly for polyamide and TPE due to the increased segmental motions at the glass transition temperature. The high value of $E’$ for polyamide was primarily due to the presence of bulky aromatic groups in the backbone chain, which explains the observed mechanical rigidity. The polyimide exhibited no transitions over the range investigated; this behavior demonstrated the mechanical

Figure 3. Optical microscopy images of the polyimide mold captured during various stages of fabrication: (a) post chemical development, (b) after wet etching of exposed nickel layer, and (c) the final structure of the polyimide mold after the dry etching step, and (d) SEM image of the actual polyimide mold.

Figure 4. Static water contact angle result measured on (a) the flat untreated polyimide sheet and (b) PFTS-treated polyimide mold surface.

Figure 5. Dynamic mechanical analysis of the polyimide mold. (a) Storage modulus ($E’$), (b) Loss modulus ($E''$), and (c) Loss tangent (tan δ) of the polyimide mold as a function of temperature.
rigidity at embossing temperatures, whereas the polymers substrates showed a decrease in modulus, indicating the polyimide’s suitability as a mold material.

The absolute values of complex viscosity vs temperature curves for the unstructured polyimide, polyamide, and TPE are presented in Figure 5d. The polymer viscosity underwent a sudden drop around 128 and 105 °C as the temperature exceeded the $T_g$ of the polyamide and TPE, respectively. There was a slight increase in the viscosity of polyamide at a temperature above 150 °C, again the result of the cold crystallization phenomenon.

The thermal stability of the polyimide mold material was evaluated from TGA (Figure 6a,b). The higher $T_{\text{max}}$ (580 °C) of the polyimide compared to the polyamide sheet ($T_{\text{max}} = 450$ °C) and TPE sheet ($T_{\text{max}} = 380$ °C) was due to the presence of bulky aromatic groups, which have a direct influence on the thermal stability. This result showed that polyimide could withstand the high temperature and nip pressures that are often encountered during the roll-to-roll hot embossing process and again supports the use of polyimide as an alternative flexible mold material.

3.2. Evaluation of Flexible Polyimide Mold by Roll-to-Roll Hot Embossing Process. The forming accuracy in roll-to-roll hot embossing is primarily influenced by roll speed, mold temperature, and nip pressure; the sheet sometimes is preheated using infrared radiation. This work employed the highest nip pressure ($P_{\text{nip}}$) of 3.7 MPa and the lowest roll speed of 0.1 m/min to expose the polyimide mold to a high-pressure environment for a longer duration. In the roll-to-roll hot embossing process, preheating of the polymer sheet reduces the temperature loss when the sheet contacts the tooling surface. Prior work, however, reported excellent replication of the injection molded microstructured surfaces at lower mold and melt temperatures, because the polyimide—metal hybrid tooling retarded heat transfer, leading to delays in melt solidification times. In addition, the microstructures had low aspect ratios (height/diameter = 0.5:1). Therefore, preheating of the sheet was not required (preliminary work.

Figure 5. Characterization of polyimide, polyamide, and TPE samples using DMA analysis, illustrating the variation of (a) storage modulus, (b) loss modulus, (c) $\tan \delta(E''/E')$ (loss tangent), and (d) absolute value of complex viscosity as a function of temperature.

Figure 6. TGA analysis of polyimide, polyamide, and TPE showing (a) derivative weight change vs temperature and (b) weight loss vs temperature.
confirmed this decision). Only the polyimide mold temperature ($T_{\text{polyimide}}$) (mounted on a steel roller) was varied to evaluate the performance of the fabricated polyimide mold. Selection of the mold temperatures was based on the absolute complex viscosity values of the two polymers, polyamide, and TPE, studied as a function of temperature (Figure 5d).

Replication of microstructures was observed on the polyamide (Figure 7) and TPE (Figure 8), indicating the effectiveness of polyimide as a mold for the R2R-HE process. Uniform and complete replication occurred at all mold temperatures in both polyamide (Figure 7a–c) and TPE (Figure 8a–c). The cross-sectional SEM image of the embossed polyamide sheet (Figure 7e) indicates that the structures were completely replicated, i.e., 100% replication efficiency, giving measured dimensions of a 14 µm diameter, 6.8 µm height, and 16.5 µm spacing (edge-to-edge), which were identical to the dimensions of the polyimide mold dimensions (diameter of 14 µm, depth of 6.8 µm, and spacing of 16.5 µm). With the commercial TPE sheet, replication efficiency also was 100%, and the embossed structures had identical dimensions to those of the polyimide mold dimensions. These dimensions and the well-defined shapes shown in Figure 8 suggest that the slower cooling with the polyimide mold enabled relaxation of the TPE material to occur during embossing, rather than after the features were separated from the mold.

The flexible polyimide mold showed the capability to withstand the high nip pressure (3.7 MPa) and temperatures (90–150 °C) for an embossing duration of 5–10 s in the R2R-HE process. The polyimide mold was also found to be durable for more than 50 embossing cycles. Preliminary work had already been performed by our group to evaluate the durability of polyimide mold (not shown in the manuscript). A low-density polyethylene sheet was used for the study to replicate microstructures. The polyimide mold was durable and maintained excellent robustness event after 100 embossing cycles at an embossing temperature (80–100 °C), nip pressure (3.7 MPa), and embossing duration (5–30 s). Further work would be needed to establish the ultimate limit of the tooling.

4. CONCLUSIONS

The continuous and large-area fabrication of micro-/nanostructures on a polymer surface by the R2R-HE process has numerous applications. The primary roadblock in the widespread application of this manufacturing technology is the availability of flexible tooling/mold materials and their fabrication approaches that are compatible with the R2R-HE process for the evaluation of different dimensions during development. The availability of low-cost tooling for preliminary development would enable more widespread applications in R2R-HE. To address this challenge, we demonstrated the fabrication of a robust flexible polyimide mold for the R2R-HE process. A polyimide mold containing holes with a diameter of 14 µm, the spacing of 16.5 µm, and a depth of 6.8 µm was successfully prepared by lithographic techniques using a maskless Direct Write system, followed by etching of the features into a commercially available polyimide sheet. The use of commercially available materials assists in
more rapid use of the mold materials. The thermal and dynamic mechanical properties of the mold material were studied to meet the criteria of thermal stability, high mechanical strength (modulus), and flexibility, which are essential for the R2R-HE process. The resulting mold was then evaluated and applied in the R2R-HE process by embossing microstructures onto two polymeric materials: polyamide and TPE sheet. The flexible polyimide mold was able to withstand the high pressure (3.7 MPa) and temperatures (90–150 °C) encountered in the R2R-HE process and to completely replicate the microfeatures in polyamide and TPE sheet. The flexible mold fabrication methodology and the associated understanding of material properties needed for the flexible molding materials provides a promising pathway for the design of new advanced flexible tooling and its implementation for large-area structuring of polymer films by the R2R-HE process.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: nischayks@gmail.com (N.K.S.).
*E-mail: Joey_Mead@uml.edu (J.M.).
*E-mail: carol_barry@uml.edu (C.F.B).

ORCID
Nischay Kodihalli Shivaprakash: 0000-0001-8315-4395
Joey Mead: 0000-0003-0631-859X

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the U.S. Army Natick Soldier RD&E Center for financial support under award W911QY-14-2-6001. The authors acknowledge the support of the John Adams Innovation Institute at the Massachusetts Technology Collaborative for the roll-to-roll hot embossing equipment and TECHNOVEL Corporation for the twin-screw extruder. N.K.S. would like to acknowledge Dr. Jinde Zhang for valuable discussions on roll-to-roll processing. Also, special thanks to the University of Massachusetts Lowell Nanofabrication Laboratory staff, James R. Goodman, Jr., and Rebecca Powers.

■ REFERENCES

(1) Kafka, J.; Larsen, N. B.; Skaarup, S.; Geschke, O. Fabrication of an all-polymer electrochemical sensor by using a one-step hot embossing procedure. Microelectron. Eng. 2010, 87, 1239–1241.
(2) Han, M.; Kim, D. K.; Kang, S. H.; Yoon, H. R.; Kim, B. Y.; Lee, S. S.; Kim, K. D.; Lee, H. G. Improvement in antigen-delivery using a one-step hot embossing procedure. Microelectron. Eng. 2009, 86, 295–298.
(3) Lee, B. K.; Hong, L. Y.; Lee, H. Y.; Kim, D. P.; Kawai, T. Replica mold for nanoimprint lithography from a novel hybrid resin. Langmuir 2009, 25, 11768–11776.
(4) Chen, W.; Ahmed, H. Fabrication of 5–7 nm wide etched lines in silicon using 100 keV electron-beam lithography and polymethylmethacrylate resist. Appl. Phys. Lett. 1993, 62, 1499–1501.
(5) Malek, C. Roll manufacturing of flexible microfluidic devices in thin polyimide and COC foils by embossing and lamination. Microsyst. Technol. 2008, 14, 851–856.
(6) Liu, C.; Li, J. M.; Liang, Y.; Peng, J.; Wang, L. D. Filling modes of polymer during submicron and nano-fabrication near glass transition temperature. J. Mater. Process. Technol. 2010, 210, 696–702.
(7) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. Imprint of sub-25 nm vias and trenches in polymers. Appl. Phys. Lett. 1995, 67, 3114–3116.
(8) Lee, S. H.; Guo, L. J. High-speed roll-to-roll nanoimprint embossing process. Lab Chip 2010, 10, 522–524.
(9) Chen, W.; Ahmed, H. Fabrication of 5–7 nm wide etched lines in silicon using 100 keV electron-beam lithography and polymethylmethacrylate resist. Appl. Phys. Lett. 1993, 62, 1499–1501.
(10) Koerner, T.; Brown, L.; Xie, R.; Oleschuk, R. D. Epoxy resins as stamps for hot embossing of microstructures and microfluidic channels. Sens. Actuators, B 2005, 107, 652–659.
(11) Pépin, A.; Youinou, P.; Studer, V.; Lebib, A.; Chen, Y. Nanoimprint lithography for the fabrication of DNA electrophoresis chips. Microelectron. Eng. 2002, 61–62, 927–932.
(12) Schi, M. B.; Kapur, S.; Iritzary, G.; Genova, V. Influence of master fabrication techniques on the characteristics of embossed microfluidic channels. Lab Chip 2003, 3, 121–127.
(13) Koo, N.; Mohamed, K.; Pin, L. T.; Guan, O. S. A review of roll-to-roll nanoimprint lithography. Nanoscale Res. Lett. 2014, 9, 320.
(14) Bender, M.; Plachetka, U.; Ran, J.; Fuchs, A.; Vratzov, B.; Kurz, H.; Glinsner, T.; Lindner, F. High resolution lithography with PDMS molds. J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.–Process., Meas., Phenom. 2004, 22, 3239–3242.
(15) Seo, S. M.; Kim, T. I.; Lee, H. H. Simple fabrication of nanostructure by a flexible polyimide mold. Microelectron. Eng. 2007, 84, 567–572.
(16) Hong, S. H.; Hwang, J. Y.; Lee, H.; Lee, H. C.; Choi, K. W. UV nanoimprint using flexible polymer template and substrate. Microelectron. Eng. 2009, 86, 932–935.
(17) Kwon, B.; Kim, J. H. Importance of molds for nanoimprint lithography: hard, soft, and hybrid molds. J. NanoSci. 2016, 2016, No. 6571297.
(18) Wu, W.; Tong, W. M.; Bartman, J.; Chen, Y.; Walmley, R.; Yu, Z.; Xia, Q.; Park, I.; Picciotto, C.; Gao, J.; Wang, S. Y.; et al. Sub-10 nm nanoimprint lithography by wafer bowing. Nano Lett. 2008, 8, 3865–3869.
(19) Lee, B. K.; Hong, L. Y.; Lee, H. Y.; Kim, D. P.; Kawai, T. Replica mold for nanoimprint lithography from a novel hybrid resin. Langmuir 2009, 25, 11768–11776.
(20) Con, C.; Zhang, J.; Jahed, Z.; Tsui, T. Y.; Yang, M.; Cui, B. Thermal nanoimprint lithography using fluoropolymer mold. Microelectron. Eng. 2012, 98, 246–249.
(21) Ahn, S. H.; Guo, L. J. High-speed roll-to-roll nanoimprint lithography on flexible plastic substrates. Adv. Mater. 2008, 20, 2044–2049.
(22) Murthy, S.; Matschuk, M.; Huang, Q.; Mardsberg, N. K.; Feidenhans'l, N. A.; Johansen, P.; Christensen, L.; Pranov, H.; Kofod, G.; Pedersen, H. C.; Hassager, O.; Taborsky, R. Fabrication of Nanostructures by Roll-To-Roll Extrusion Coating. Adv. Eng. Mater. 2016, 18, 484–489.
(23) Veltien, T.; Bauerfeld, F.; Schuck, H.; Scherbaum, S.; Landesberger, C.; Bock, K. Roll-to-roll hot embossing of micro-structures. Microsyst. Technol. 2011, 17, 619–627.
(24) Lee, J.; Park, S.; Choi, K.; Kim, G. Nano-scale patterning using the roll typed UV-nanoimprint lithography tool. Microelectron. Eng. 2008, 85, 861–865.
(25) Guo, L. J. Nanoimprint lithography: methods and material requirements. Adv. Mater. 2007, 19, 495–513.
(26) Peng, L.; Deng, Y.; Yi, P.; Lai, X. Micro hot embossing of thermoplastic polymers: a review. J. Micromech. Microeng. 2013, 24, No. 013001.
(27) Brinksmeier, E.; Gläbe, R.; Schönemann, L. Diamond micro chiseling of large-scale retroreflective arrays. Precis. Eng. 2012, 36, 650–657.
(28) Huang, M. S.; Chiang, Y. C.; Lin, S. C.; Cheng, H. C.; Huang, C. F.; Shen, Y. K.; Lin, Y. Fabrication of microfluidic chip using micro-hot embossing with micro electrical discharge machining mold. Polym. Adv. Technol. 2012, 23, 57–64.

(29) Yao, T. F.; Wu, P. H.; Wu, T. M.; Cheng, C. W.; Yang, S. Y. Fabrication of anti-reflective structures using hot embossing with a stainless steel template irradiated by femtosecond laser. Microelectron. Eng. 2011, 88, 2908–2912.

(30) Schelb, M.; Vannahme, C.; Kolew, A.; Mappes, T. Hot embossing of photonic crystal polymer structures with a high aspect ratio. J. Micromech. Microeng. 2011, 21, No. 025017.

(31) Chung, C. K.; Sher, K. L.; Syu, Y. J.; Cheng, C. C. Fabrication of cone-like microstructure using UV LIGA-like for light guide plate application. Microsyst. Technol. 2010, 16, 1619–1624.

(32) Mappes, T.; Worgull, M.; Heckele, M.; Mohr, J. Submicron polymer structures with X-ray lithography and hot embossing. Microsyst. Technol. 2008, 14, 1721–1725.

(33) Chung, C. K.; Syu, Y. J.; Wang, H. Y.; Cheng, C. C.; Lin, S. L.; Tu, K. Z. Fabrication of flexible light guide plate using CO2 laser LIGA-like technology. Microsyst. Technol. 2013, 19, 439–443.

(34) Tsai, S.-W.; Lee, Y. C. Fabrication of ball-strip convex microlens array using seamless roller mold patterned by curved surface lithography technique. J. Micromech. Microeng. 2014, 24, No. 015014.

(35) Rank, A.; Lang, V.; Lasagni, A. F. High-Speed Roll-to-Roll Hot Embossing of Micrometer and Sub Micrometer Structures Using Seamless Direct Laser Interference Patterning Treated Sleeves. Adv. Eng. Mater. 2017, 19, No. 1700201.

(36) Striegel, A.; Schneider, M.; Schneider, N.; Benkel, C.; Worgull, M. Seamless tool fabrication for Roll-to-Roll microreplication. Microelectron. Eng. 2018, 194, 8–14.

(37) Lang, V.; Rank, A.; Lasagni, A. F. Large Area One-Step Fabrication of Three-Level Multiple-Scaled Micro and Nanostructured Nickel Sleeves for Roll-to-Roll Hot Embossing. Adv. Eng. Mater. 2017, 19, No. 1700126.

(38) Tsai, S.-W.; Chen, P. Y.; Lee, Y. C. Fabrication of a seamless roller mold with wavy microstructures using mask-less curved surface beam pen lithography. J. Micromech. Microeng. 2014, 24, No. 045022.

(39) Wu, C. C.; Hsu, S. L. C.; Lo, I. Fabrication and Application of Polyimide Plastic Molds for Nanoimprint Lithography. J. Nanosci. Nanotechnol. 2010, 10, 6446–6452.

(40) Kim, Y. Investigation of micro and nanoscale surfaces replication using injection molding. Doctoral Dissertation; University of Massachusetts Lowell, 2012.

(41) Banerjee, S. S.; Bhowmick, A. K. Novel nanostructured polyamide 6/fluoroelastomer thermoplastic elastomeric blends: Influence of interaction and morphology on physical properties. Polymer 2013, 54, 6561–6571.

(42) Ridhore, A.; Jog, J. Synergistic mechanical response of Nylon 6/Trogamid T blends. J. Appl. Polym. Sci. 2013, 129, 65–72.

(43) Song, J. W.; Loifgren, J.; Hart, K. D.; Tsantinis, N.; Paulson, R.; Hatfield, J. N. Aromatic Nylons for Transparent Armor Applications; Army Natick Soldier Research Development and Engineering Center: MA, 2006.

(44) Kodihalli Shivaprakash, N.; Zhang, J.; Panwar, A.; Barry, C.; Truong, Q.; Mead, J. Continuous manufacturing of reentrant structures via roll-to-roll process. J. Appl. Polym. Sci. 2019, 136, 46980.