Fabrication of Rough Polymer Surfaces Exhibiting Anti-reflective Properties

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ABSTRACT
We have demonstrated some facile ways to fabricate the large area polymer surfaces with varying roughness followed by studying their anti-reflective properties. One of the approaches is based on electrospun nanofibers deposited on a substrate in an uneven non-woven matrix. This electrospun fabric was used as a master template to fabricate the negative replica of the fibers by soft lithography generating the roughness in polydimethylsiloxane (PDMS) surfaces. The second approach is based on biomimicking of flower petals. Petals are used as a master template to transfer surface features with hierarchical roughness over PDMS surface using replica moulding. As fabricated polymer surfaces with varied roughness have then tested for their anti-reflective properties using UV-VIS spectroscopy over a wide range of wavelengths and angles of incidence of light. These measurements show near zero reflection of patterned PDMS surfaces as compared to planar PDMS. This omnidirectional broadband anti-reflection behaviour of polymer surfaces can be used in wide variety of engineering applications including in solar cells.

INTRODUCTION
Surfaces which suppress reflection are known as anti-reflective and are widely used in lot of engineering applications such as optical devices, light emitting diode and solar cells [1-3]. Antireflection can be achieved using thin film coatings however with some limitations like radiation damage due to thermal gradient between different layers, adhesion problems within multiple thin film layers and therefore, cannot be used for a broad range of incident light. Taking inspiration from nature, several studies have been carried out on certain species of moths, as their corneal surface has regular hexagonal arrays of sub-micron structures [4-5]. Further certain species of butterflies have multiscale structures on their wings which exhibits antireflective properties [6-7]. However fabrication of those multiscale structures is either limited by small area constraint or cost associated with use of highly sophisticated micro- and nano-fabrication tools [8-10]. In the present work, we have demonstrated a simple approach to fabricate large area anti-reflective polymer surfaces by inducing roughness at different length scale. First approach is based on exploiting the roughness of nanofibers deposited in a non-woven matrix by electrospinning [11-12]. Electrospun nanofiber mat has been used as a master template to fabricate the negative replica of the fibers in polydimethylsiloxane (PDMS) using soft lithography. By varying the fiber morphology from long continuous fibers to only beads, we have fabricated negative PDMS replicas with surface roughness varying over an order of magnitude in length scale. In second approach, biomimicking has been demonstrated as another way to fabricate rough polymer surfaces over a large area [13-14]. Here we have chosen flower petals of a plant, Euphorbia milii, as a master template. Euphorbia milii petal is ultrahydrophobic due to the presence of multiscale surface features leading to hierarchical roughness. These surface features were then successfully transferred using replica molding to prepare large area rough PDMS surfaces. As-patterned PDMS surfaces with varying roughness have then be tested for their anti-reflective properties using UV-Vis spectroscopy over a wide range of wavelengths (400-700nm) and at incidence angles ranging from 30° to 70°. These measurements show that reflectance has been reduced significantly (less
than 0.1%) as compared to planar PDMS surfaces with no surface texturing. This omnidirectional broadband anti-reflection behaviour of polymer surfaces may be attributed to multiple internal reflections and light trapping within the micro textures present on their surfaces resulting from surface roughness. We believe that facile approaches as depicted here to fabricate large area rough polymer surfaces may provide cost effective solution in the manufacturing of anti-reflective surfaces for wide variety of engineering applications including in solar cells [1-3].

EXPERIMENTAL DETAILS

Materials

Sylgard 184 prepolymer solution (consisting of two part PDMS elastomer and a cross-linking agent) was purchased from Dow corning, India. Cellulose acetate (acetyl content 39.8%, molecular weight 29000) was purchased from Sigma Aldrich, India. N, N- Dimethylacetamide (DMA), acetone, chloroform, all AR grade, were purchased from Merck India.

Method 1 (Electrospinning)

A known amount of cellulose acetate was dissolved in 2:1 (v/v) ratio of DMA and acetone by magnetic stirring at room temperature to obtain a clear solution. This solution was then filled in a plastic syringe having stainless steel needle attached to its tip. A high voltage supply was then connected to the needle. Aluminium foil was wrapped on a grounded copper collector for collecting the fibers. The details on electrospinning set up can be found elsewhere [13]. Electrospinning was done for 30 minutes on aluminium foil used as a substrate with following set of parameters- applied voltage: 10kV, distance between syringe needle and collector: 10cm., syringe needle: 24 gauge (ID 0.31mm), feed rate: 1µl/m. To fabricate the fibers and only bead morphology by electrospinning of cellulose acetate, solution of different concentration, 16 and 8 wt.% was used respectively with other set of parameters unchanged.

The electrospun fabric with different morphology was then used as a master template to prepare negative PDMS replicas as shown in Figure 1A.

Method 2 (Biomimicking)

In second approach as mentioned, E. Milii flower petal was used as a master template. We first cut the flower petal into small pieces of dimensions 5 cm x 5 cm and dried at 40°C for 60 min to remove any moisture.

Fabrication of negative PDMS replicas

First, PDMS solution was prepared using 10:1 weight ratio of Sylgard 184 polymer elastomer and cross-linking agent. There was a slight different in experimental protocols for fabricating negative PDMS replica using two different templates. In case of electrospun fabric used as master template, we first poured the pre-polymer PDMS solution inside a glass petri dish followed by de-aeration in vacuum dessicator to remove trapped air bubbles and cured it partially by heating it in hot air oven at 80°C for 1 h. Once the PDMS is partially cured, we placed the electrospun fabric master template on to it followed by complete curing at same temperature for another 12 h. In case of natural E-milli flower petal, the samples were first fixed inside the clean glass petri dishes using a thin double side adhesive tape before pouring the pre-polymer PDMS solution. Samples were then de-aerated in vacuum desiccator followed by curing at 80°C for 12 h.

Later, completely cured PDMS samples were swelled by exposing into chloroform for 30 min for easy removal of template and to produce negative PDMS replica with features imprinted
on it as shown in Figure 1B. As prepared negative PDMS replicas were then dried in air at room temperature for 60 min before using further for their analysis.

**Characterization**

Surface morphology of original template and negative PDMS replicas were analysed using table top scanning electron microscopy (ProX Model, Phenom World). UV-Vis spectroscopy (Lambda-35 model, Perkin Elmer) measurements were carried out for wavelength varying over 400-800 nm and angle of incidence 30° to 70°.

**RESULTS AND DISCUSSION**

**Surface Morphology**

**Figure 1.** Schematic representation of preparation of negative PDMS replicas from (A) electrospun fabric and (B) E. Milii flower petal using replica molding.

**Figure 2.** SEM images of original electrospun beads (a1, b1), fibers (c1, d1) and negative PDMS replicas of beads (a2, b2) and fibers (c2, d2) respectively.
Figure 2 summarizes the surface morphology of as-spun cellulose acetate beads (a1, b1) (8 wt.% solution) and long continuous fibers (c1, d1) (16 wt.% solution). Images in second row (a2-d2) are for negative PDMS replicas. We can clearly observe that morphology of electrospun cellulose acetate fibers and beads were successfully replicated on to PDMS surface. The average diameter of electrospun beads and fibers were measured to be 350 ± 124 nm and 417 ± 67 nm respectively.

Similar observations were made for E.milli flower petal and its negative PDMS replica (Figure 3). Original E. Milii petal possesses multi scale structures as shown in Figure 3 (a1-c1) at different magnification. Micro-textures surface of petal while observed at higher magnification (Figure 3c1) shows tiny wax like structures with average feature size 210 nm. Negative PDMS replica as fabricated also showed similar patterns at various magnifications (Figure 3a2-c2). At higher magnification (Figure 3c2), we observed holes like structures with average feature size 340 nm which are inverse protrusions to that of original petal features.

![Figure 3](image)

**Figure 3.** SEM images of original E. Milii petal (a1-c1) and negative PDMS replica of petal (a2-c2) at different magnification.

**Optical Properties**

Generally, plant absorb sun light through its leaves and petal for their photosynthesis process. They process electromagnetic radiation in the blue (400-480 nm) spectral range and yellow (550-770 nm) spectral range. The surface textures of leaves and petals play an important role in absorption, transmission and reflection of sun light from their surfaces [15-16]. As observed and discussed above (Figure 2 and 3), we have fabricated textured polymer surfaces with varying roughness and then tested for their optical properties in terms of % reflection and % transmission as summarized in Figure 4 and 5 respectively. Plain PDMS surface was used as reference in these measurements. In case of electrospun fibers (Figure 4a), we observe that as compared to plain PDMS surface which shows reflection from 0.35-0.38%, negative PDMS replica of beads and fibers show reflection values 0.15 and 0.25 % respectively for all wavelength of light used (400-700 nm). The angle of incidence of light in all these cases was maintained 30°. Further, reflection values were measured by varying the angle of incidence while keeping the wavelength of light constant (700 nm). As shown in figure 4b, plain PDMS surface shows a reflection of 0.39% at 30° which gradually increased to almost 1% at 70°. However interestingly, negative PDMS fiber and bead replicas showed almost 0.2 % and 0.1 % reflection respectively irrespective of the angle of
incidence. For complete understanding of optical behaviour from these patterned polymer surfaces, we further measured the transmission values at a normal angle of incidence of light of wavelengths ranging from 400 nm to 800 nm (Figure 4c). Plain PDMS surface shows a transmission of about 60% to 65% in all wavelengths while negative PDMS fiber and bead replicas surface showed significant decrease in transmission values. For fiber replica, it was measured to be nearly 35% which was further reduced to 10% for beads based PDMS replicas.

Figure 4. Percentage reflection as a function of (a) wavelength of light (b) angle of incidence of light while (c) shows the transmission of light as a function of wavelength of light for electrospinning based negative replicas of PDMS.

A similar trend was observed for reflection and transmission values for the negative PDMS replicas as fabricated using E.milli flower petal as master template (Figure 5). The original E.milli flower petal shows a reflection of 0.03% up to 510nm however there is a gradual increase in reflection since the pigments in the petal absorb the blue spectral region (400nm to 480nm) and green spectral region (480nm to 550nm) and reflect the yellow and red region (550nm to 700nm) (Figure 5a). Importantly, we observed that biomimicked petal surface in PDMS showed near zero reflection (0.03%) for full visible range of wavelength of light. Here, it is clearly observed the role of surface textures in controlling the optical properties. In absence of pigments, it is only surface texturing which determines their reflection behaviour. Further we varied the angle of incidence of light and measured the reflection values (Figure 5b). The original petal shows a reflection of 0.2% at all angles of incidence of light while textured PDMS surface shows near zero reflection. On further examining the transmission properties (Figure 5c), we observed that both original flower petal and negative PDMS replica surfaces transmit only 4% light as compared to 60-65% in case of plain PDMS surface.

Figure 5. Percentage reflection as a function of (a) wavelength of light (b) angle of incidence of light while (c) shows the transmission of light as a function of wavelength of light for negative replicas of PDMS prepared by biomimicking E.mill flower petal
These results confirm the near-zero reflection behaviour of patterned PDMS surfaces with varying degree of roughness. Primarily this behaviour may be attributed to multiple internal reflections arising from the micro- and sub-micron sized textures present on their surfaces. Further due to negative replica of features (beads, fibers, protrusions), textured PDMS surface is having hole like structures which may be reflecting the light multiple times inside these materials and thereby lengthening the travel path of light leading to enhanced absorption.

CONCLUSION

In the present study, we have demonstrated two facile approaches to fabricate the large area rough polymer surfaces which exhibit antireflective properties over a wide range of wavelength and angle of incidence of light. A planar polymer surface and original bio-template were used as reference to clearly understand the role of surface textures on optical properties. The approaches depicted here in this work are not only easy and cost effective but also may be applicable to large number of polymers. Further a negative PDMS replica can not only be used multiple times as template but can be used to produce positive replica in other polymers too. This omnidirectional broadband anti-reflection behaviour in polymer surfaces due to surface texturing may be used in wide variety of engineering applications such as optical displays and solar cell panels.

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REFERENCES