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Fabrication of nanostructured polymers by laser-assisted hot embossing for biological and optical applications

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Abstract

Rapid manufacturing of micro- and nano-structured polymers was achieved by laser-assisted hot embossing technique. Metallic mold surfaces containing fabricated nanostructures have been replicated using thermoplastics such as polystyrene (PS) and cyclic olefin copolymer (COC). The applied nano-sized structures were fabricated on stainless steel using ultrafast laser radiation to generate Laser-Induced Periodic Surface Structures (LIPSS) for control of wettability and bio-compatibility. Furthermore, electroformed nickel shims containing nanostructures were replicated using COC for subsequent surface-enhanced Raman spectroscopy (SERS) measurements. It was demonstrated that laser-assisted moulding of thermoplastics offers a cost-efficient and flexible technique for the production of functional polymeric surfaces with nano-sized features.

Keywords— laser-assisted hot embossing, Surface Enhanced Raman Spectroscopy, Laser-Induced Periodic Surface Structures, surface modification

1. Introduction

The achievement of a rising life expectancy brought us the challenge of an aging population and will require a functional health care workforce to deal with this unprecedented issue [1]. Therefore new biological and medical processes have to be implemented to achieve fast and cost-efficient treatments for patients. Surface modifications such as wettability and hydrophobicity have shown to improve the biocompatibility of *in vitro* medical devices which have been developed during the last twenty years [2]. Disposable thermoplastics are commonly used in life sciences, point of care and veterinary industries. To modify the surface of these polymers injection moulding, thermoforming and hot embossing are state of the art technologies [3,4]. At Karlsruhe Institute of Technology (KIT) laser-assisted hot embossing was developed for enabling fast replication of micro- and nanostructured polymeric surfaces. Durable mould inserts are made of silicon, glass or metal. This approach provides a low-cost surface texturing with a variety of applications in the field of optics, medicine, and biology. For laser-assisted hot embossing the laser intensity is controlled by a pyrometer setting a temperature above the glass transition temperature of the transparent thermoplastic to penetrate the glass plate and polymer to heat the mould behind it locally. It therefore generates a thermodynamic mass transfer due to a surface tension gradient inside the polymer to replicate the nanostructures onto the thermoplastic as the polymer is clamped between the glass plate and the mould [5]. Zheng et al. [6] could fabricate LIPSS nanostructures on metallic surfaces for battery applications using a femto second laser system. In our approach the replication of different nano-sized structures can be easily replicated by using a high power diode laser as a radiation source for laser-assisted hot embossing. Here the fabrication of LIPSS nanostructures and their replication via laser-assisted hot embossing is demonstrated. Furthermore, e-beam written periodic nanostructures for SERS application were replicated with COC and tested regarding the optical performance.

2. Experimental

2.1. Fabrication of laser-induced periodic surface structures

The generation of LIPSS was realized using an ultrafast fiber laser (Tangerine, Amplitude Systèmes, France) with an average power of 35 W and a maximum pulse energy of 175 µJ operating at wavelengths of 1030 nm, 515 nm, and 343 nm (TEM00 with M^2 <1.2). Materials processing was performed with PS450-TO laser micromachining system (Optec s.a., Belgium). Processing can be realized for repetition rates from 1 Hz up to 2 MHz and tunable pulse durations from 380 fs up to 10 ps. Stainless steel (1.4435) was treated near the energy threshold to form LIPSS nanostructures. Therefore an average laser power of 80-120 mW was used with a laser scanning speed between 10-50 mm/s while the pitch distance was set in a range of 8-15 µm.

2.2. Laser-assisted hot embossing of polymers

The laser-assisted hot embossing process was carried out by a 100 W high power diode laser (LM100, Dr. Mergenthaler GmbH, Germany) operating at a wavelength of 938 nm. The laser head is attached to an fiber coupled infrared pyrometer (EP004, Dr. Mergenthaler GmbH, Germany). The laser scanner (LH501-M, Raylase, Germany) has a processing area of 195mm x 195 mm and a working distance of 220 mm. A pneumatic stage was used to clamp the polymer material between the nanostructured stainless steel or Ni shim (as mould insert; fabricated by combination of e-beam lithography and electroforming [7]) a high transparent quartz glass substrate. The glass substrate is faced to the laser scanning optics and the applied clamp pressure is about 2 bar which corresponds to a clamping force of around 120 N. Fig. 1 shows the different processing steps involved. As polymer materials, polystyrene (PS, ST313120, Goodfellow GmbH, Germany) and cyclic olefin copolymer (COC, 6013M, Topas, Germany) were used for replication of periodic and LIPSS nanostructures. PS and COC had a thickness of 1.2 mm and 175 µm, respectively. Both types of polymers are of great interest for lab-on-chip application due to their optical properties (PS, COC) and biocompatibility performance (PS). Due to a low fluorescence, COC provides optimal conditions for SERS. The pyrometer controlled laser intensity was set to 164 °C. The temperature can be maintained with an accuracy of ±5 °C while the laser scanning velocity was fixed to 5 mm/s. Replication of PS was carried out by maintaining the laser power at 10-12 W and applying a laser scan velocity of 70 mm/s.

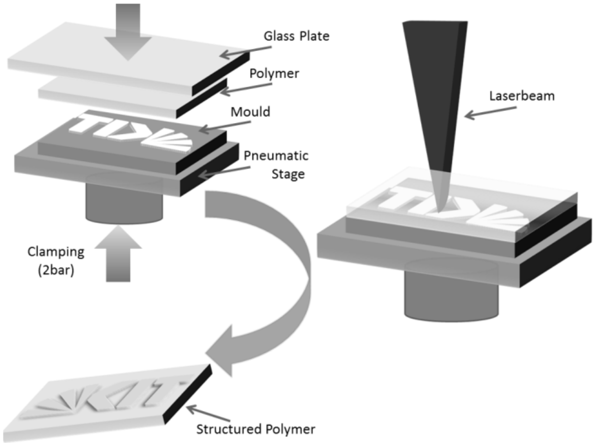

Figure 1. Schematic view of the laser-assisted hot embossing process

3. Results

3.1. Modified adhesion due to nanostructured polymers

Fast replication of nanostructured stainless steel surface could be accomplished by using polystyrene as shown in Fig. 2. Polymer surface textures can be controlled on micro- and nano-meter scale. The aim is to control biocompatibility regarding cell, protein and bacteria adhesion which was already evaluated for stainless steel surfaces containing LIPSS [8].

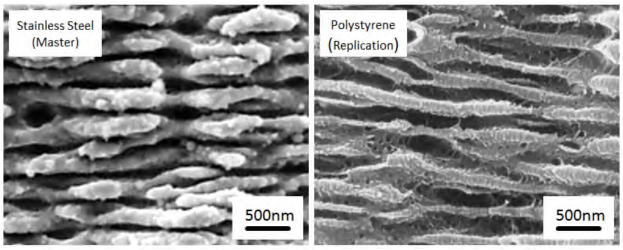

Figure 2. SEM of stainless steel mold and replicated LIPSS nanostructures on polystyrene surface.

3.2. Surface enhanced Raman spectroscopy

A patterned array of nanostructures on a Ni shim produced by electroplating was successfully replicated using COC as polymer material. The nano-sized features are shown in Fig. 3. The positive impact of gold coated COC nano arrays on the SERS enhancement was reported elsewhere [9]. Here a 10 µM aqueous solution of rhodamine 6G as exemplary analyte was used. The SERS measurement was performed with a 638.2 nm helium-neon laser at 0.9 mW as excitation source. The diameter of the copied nanopillars are 200 nm while there height is approx. 100 nm.

4. Summary, conclusion and future work

It was shown that laser-assisted hot embossing is a versatile and flexible approach for the replication of polymeric surfaces with lateral accuracy down to the nanometer range. Furthermore, this rapid process could be used to establish nano-ripples on PS surfaces. Prior to laser-assisted hot embossing, the corresponding mould insert made of steel was structured by ultrafast laser radiation (LIPSS). It can be shown that laser-assisted hot embossing can realize a variety of biomedical or lab-on chip applications with low technical effort (no vaccum, short processing time). Further process optimization will be necessary for transfer of the process parameters regarding additional polymer materials and an upscaling to larger footprint areas. Different types of mould insert material and structure sizes (e.g., aspect ratio) will require a better understanding of the material flow as function of material properties and temperature field. Besides the demonstration on functional lab-on-chip devices containg SERS, the impact of nanostructured surfaces on wettability, cell and bacteria adhesion will be studied in detail.

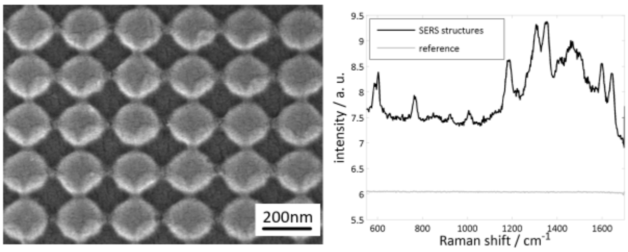

Figure 3. SEM of COC nanostructures replicated by laser-assisted hot embossing using a Ni shim mould insert (left) and the SERS spectra of 1µM Rh6G solution on the gold coated COC structures and on an unstructured gold surface as reference.

Acknowledgments

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