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Microcontact printing of polyelectrolyte multilayer thin films: Glass–viscous flow transition based effects and hydration methods

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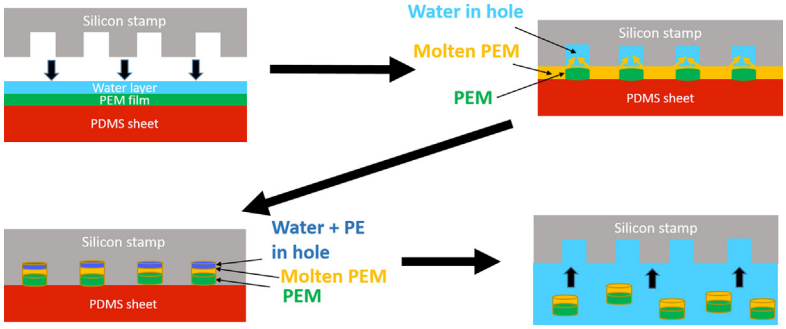
HIGHLIGHTS

- Glass–viscous flow transition effects influences the quality of PEM patterns during printing.
- PEM that dissolves within stamp structure increases osmotic pressure.
- Osmotic pressure can be used to expel printed PEM structures from stamps.
- Cold water vapour from a humidifier can be used for humidifying PEM.
- Active printing area necessary for printing PEM not total stamp area.

GRAPHICAL ABSTRACT

Micro and nanostructured surfaces and samples are of fundamental importance for electronics, tissue engineering and drug delivery. The effect of glass–viscous flow transition on thin polymer films for microcontact printing was investigated by the example of polyelectrolyte multilayers depending on the softening method (cold versus hot solvent) and for different temperatures in relation to the glass–viscous flow transition point. Interestingly PEM structures can not only be printed but also be expelled from stamps in aqueous solution when the stamp is removed. This is due to emerging osmotic pressures created by dissolving PEM at temperatures exceeding the PEM glass transition point.



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ABSTRACT

Micro and nano-patterned surfaces are important for many applications ranging from antibiofouling over tissue engineering to electronics. Often the incorporation of functional entities is of interest. Polymer coatings especially polyelectrolyte multilayer (PEM) films and patterns are materials offering a large variety of tuning and engineering. The PEM pattern printing quality bases not only on the surface force balance but also in the way the PEM is softened, which can be done by printing the PEM in water, using an ultrasound humidifier or by exposing the film to (hot) water vapor. In this publication it is shown, that cold water vapor from an ultrasound humidifier or direct printing in water is superior to steam evaporation onto PEM thin films as humidification method. In addition the capillary pressure of the patterns within the stamp and the glass–viscous flow transition point of the PEM thin film are the significant parameters for PEM printing. This is because the PEM can surpass the glass–viscous flow transition point due to the shear forces and be sucked into the stamp microwells (or holes) preventing a structure replication. Under high temperatures and in aqueous conditions, the PEM can be expelled from the microwells due

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to the osmotic pressure produced by the counter ions of PEM in glass–viscous flow state and dissolving polyelectrolyte if a PEM with counter ion based charge balance is used.

1. Introduction

The creation of micro and sub-microstructures is of fundamental interest for numerous applications ranging from biosensors [1] over electronic [2] to antifouling [3,4] surfaces. Out of a large variety of potential techniques micro and sub-microstructures can be conveniently produced by microcontact printing (μCP) [5]. Within the last 20 years thin polymer films produced by the layer-by-layer [6] (LbL) bottom up approach gained significant interest. These polymer films comprise out of electrostatically charged polymers called polyelectrolyte (PE) and are assembled in an alternating manner to a multilayer (PEM). The PEM thickness can be controlled down to sub-nanometer precision and even contain living cells and other functional entities like nanoparticles [7,8]. For the design of real or reproduced tissue or drug delivery systems [9] it is of fundamental importance to control the PEM structure and shape. One method is the use of templates [9], another one was introduced by Hammond and Park in the year 2004 by simply μCP PEM thin films using a polydimethylsiloxane (PDMS) stamp (silicone rubber stamp). Since then the system was used by a variety of researchers [10–13] from different groups including our own, which also tried to explain the effects responsible for μCP.

Since a lot of research has been done to explain the PEM printing effects, we summarize the current state of the art of μCP on a small overview of existing explanations and problems in the supporting information (SI). Briefly, μCP of a solid PEM film printed at low pressures is based on surface forces and PEM mechanical properties, while high pressure can cause a liquefaction of the PEMs [11,13–15]. The printing limit of PEM is PEM surface energy and line tension and not PDMS structure based [5,13]. In case applying high pressure the detailed effects are not fully understood especially for systems containing PEM in viscous flow state, where reports are very scarce, no temperature or different pressures and PEM composition are available. Park et al. was to the knowledge of the authors the first to investigate the effect of capillary pressure on the printing quality, while the Shen group reported PEM flowing effects at high pressure printed PEM [11,16].

It is worth to point out that not only PDMS stamps were utilized for low pressure condensed PEM printing but some groups used a dissolvable PMMA stamp instead of PDMS stamps [17–19]. In this case the consideration of the relevant surface forces is not necessary because the PMMA can be dissolved in organic solvent releasing the PEM patterns. Other groups, on the contrary, focused on transfer methods, without the need to dissolve the PMMA stamps [20]. During the printing process the osmotic and capillary forces are similar for PMMA and PDMS based stamps and just the force strengths differ. Therefore the results presented in this publication are extendable to PMMA stamp based systems.

In this report, we study the printing of PEM films with short printing times in the range of seconds, and pressures up to 50 g/cm^2, whereby the focus lies on the glass–viscous flow transition effects of PEM films and how to prevent PEM from undergoing glass–viscous flow transition. We also discuss effects of the printing time, which can also affect the flow of PEM in viscous flow state, an effect ignored in other publications trying to print liquefied PEM systems [11].

2. Experimental

2.1. Production of PEM thin films

The utilized PEM thin films were produced by spraying deposition method [21] onto flexible silicone rubber sheets (PDMS) (Dow Corning Midland, USA) which was produced by mixing component A and B in 10:1 ratio, degassing it for 30 min in vacuum and curing it for 2 h at 70 °C. The air–PDMS interface was used for PEM assembly. The spraying time for each solution including rinsing water was 6 s with a distance between spraying bottle and sample of 15 cm. The used water was ultrapure water (18.2 MOhm cm, Elga Labwater, Beijing, China). The spraying cans were DC (Duennschicht Chromatographie) Spruehflaschen (type Air Boy, Nr. 0110.1) purchased from Carl Roth, Germany. The used polyelectrolytes (PE) were polyacrylic acid (PAA) with a molecular weight (MW) of 1800 g/mol, polystyrenesulphonate (PSS, MW 70,000 g/mol), poly(diallyldimethylammonium chloride) (PDDA, MW 100,000-200,000 g/mol), polyallylamine hydrochloride (PAH, MW 56,000 g/mol), polyethylenimine (PEI, MW ~750,000 g/mol). The FITC (fluoresceine isothiocyanate), which was chemically linked to PAH, according to ref. [22] was along with the PE purchased from Sigma, St. Luis, USA. The PE concentration for all PE solutions was 0.5 g/L with an ionic strength of 0.5 Mol/L (NaCl, Chemical Reagents, Tianjin, China).

The PE solution spraying sequence, which determines the PEM build-up structure, was:

1. PEI(PSS-PDDA)$_4$(PSS-PAHFITC)$_2$;
2. PEI(PSS-PDDA)$_4$(PSS-PAHFITC)$_2$PSS;
3. PEI(PAA-PAH)$_4$(PAA-PAHFITC)$_2$;
4. PEI(PAA-PAH)$_4$(PAA-PAHFITC)$_2$PAA.

Whereby the terminal layers of samples 1 and 3 are positively and samples 2 and 4 are negatively charged. This allows a defined comparison of the effect of internal charge ratio and surface charge on the PEM printing properties at different temperatures. Printing pressures of 0, 10, 20, and 50 g/cm^2 were used. The investigated temperatures were 22, 25, 30, 34 and (for preliminary studies) 37 °C with a printing time of 5 or 45 s.

2.2. PEM softening methods

Three different PEM softening methods were compared:

1. After the PEM was produced it was dried with N_2 first, then humidified with water vapor produced from water heated to 65 °C for 5 s (distance 1 cm), then the stamp was pressed onto the PEM film with above parameters, then removed.
2. After the PEM was produced it was dried with N_2 then humidified with water vapor from an ultrasound humidifier (Yadu SC-M20, Henan Yadu Industrial Co. Ltd., Henan, China) 1 cm distance, 5 s evaporation time, power wheel adjusted to a position which is ~10° above off. Afterwards the stamp was pressed onto it with the above stated parameters, and then removed.