MICRO/NANOPATTERNING OF POLY(ETHYLENE NAPHTHALATE) VIA PATTERN REPLICATION TECHNIQUES: A ROBUST ALTERNATIVE TO POLY(METHYL METHACRYLATE).

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The use of polymers is becoming increasingly common in the production of biomedical devices. For such devices we have investigated the forming of polymer micro and nanostructures in poly(ethylene naphthalate) (PEN), using imprint techniques such as hot embossing (HE) [1] and nanoimprinting (NI) [2], and compared the performance of PEN with a commonly used polymer for imprint techniques, poly(methyl methacrylate) (PMMA).

PEN is a semi-crystalline, thermoplastic polyester, available since 1948 [3], with good mechanical properties and a working temperature up to 155°C [4]. It is resistant to dilute acids and organic solvents, and has good optical clarity and UV radiation absorbance [5]. At physiological conditions PEN is stable and biocompatible. As a consequence, it already has applications in the production of food containers, in particular plastic bottles, which can withstand the temperatures required for sterilisation. Its inherent strength and dimensional stability also means PEN is used for fibres and films where low shrinkage and elongation properties are required [6]. In comparison, PMMA is an amorphous, thermoplastic polymer, which is commonly used for polymer forming due to its inertness and highly applicable physical properties (e.g. with a low thermal expansion coefficient). However, PMMA has poor temperature and solvent resistances, which puts it at a disadvantage when considering some chemical and biological applications.

HE and NI experiments have been completed on both polymers using master stamps with feature dimensions ranging from 50 μ m to 200 nm. Rough surface features have been imprinted in the polymer surfaces via HE using a commercially available frosted glass master (Fig. 1) and a F₂ doped SnO₂ coated glass master (Fig. 2). The frosted glass produces imprinted features up to 50 μ m deep in both of the polymers, and even replicates the crystal structure and the terracing seen in the HF etched surface of the master. The images of the SnO₂ replicas show features with dimensions of approximately 500 nm due to the SnO₂ crystals. In each case, comparable roughness has been achieved for the polymers compared to the masters: 2.65 μ m for the frosted glass and 40 nm for the SnO₂ coated glass. Hot embossing conditions for each of the polymers with each of the masters are given in table I.

NI has been completed using a master milled using focussed ion beam apparatus from the Si_3N_4 layer of a $Si_3N_4/SiO_2/Si$ substrate (Fig. 3). The master contains an ordered series of structures, ranging in size from 20 x 20 µm to 20 µm x 200 nm, and with a depth in each case of 100 nm, which are reproduced in the polymers using the conditions in table II.

Although the PEN requires more forceful imprinting conditions than PMMA, its ability to form micro/nanostructures allied to high temperature stability and superior chemical resistance, compared to PMMA, suggest that it could be a useful material for the production of, or for incorporation into, micro and nanostructured devices for biomedical applications. This same temperature resistance allied to the dimensional stability may also make PEN useful as a substrate for the production of devices containing micro/nanoelectrodes.

References:

- [1] M. Hekele and W. K. Schomberg, J. Micromech. Microeng. 14 (2004) R1-R14.
- [2] C. M. Sotomayor-Torres, S. Zankovych, J. Seekamp, A. P. Kam, C. Clavijo Cedenõ, T. Hoffmann, J. Ahopelto, F. Reuther, K. Pfeiffer, G. Bleidiessel, G. Gruetzner, M.V. Maximov and B. Heidari, Mater. Sci. Eng. C 23 (2003) 23-31.
- [3] R. Jakeways, J. L. Klein and I. M. Ward, Polymer **37** (1996) 3761-3762.
- [4] T. Higashioji, T. Tsunekawa and B. Bhushan, Trib. Int. **36** (2003) 437-445.
- [5] I. Ouchi, I. Nakai and M. Kamada, Nucl. Instr. Meth. Phys. Res. B 199 (2003) 270-274.

Figures and tables:



Fig. 1. White light interferometer images of (*a*) the frosted glass master, and (*b*) PMMA and (*c*) PEN hot embossed surfaces (image dimensions = $94.6 \times 124.4 \mu m$).



Fig. 2. SEM images of (a) the SnO2 coated master, and the (i) pristine and (ii) hot embossed surfaces of (b) PMMA and (c) PEN (bar = $2 \mu m$).



Fig. 3. SEM images of (*a*) the milled Si_3N_4 master, and (*b*) PEN nanoimprinted surface (bar = 20 µm). The * marks the position of the 20 x 20 µm structure. (PMMA image unavailable at this time).

Table I. Hot embossing conditions						Table II. Nanoimprinting conditions				
Polymer	Master	Embossing conditions			Cooling	Polymer	Master	Nanoimprinting conditions		
		T / °C	P / Nm ⁻²	t / s	T / °C			T / °C	P / Nm ⁻²	t / s
PMMA	Frosted	120	2.50×10^{6}	600	80	PMMA	Squares	120	5.00×10^{6}	300
	SnO_2	120	4.17×10^{6}	600	80	PEN	Squares	150	6.00×10^{6}	600
PEN	Frosted	200	1.88×10^{7}	1200	80					
	SnO_2	200	3.13×10^{7}	1200	80					