## Recovery prevention via pressure control in T-NIL

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Polymer recovery is a typical phenomenon observed during thermal nanoimprint (T-NIL) in cases where wide patterns are imprinted into thin layers<sup>1,2</sup>. It manifests the polymers' visco-elasticity. When deformed, the polymer first reacts elastically, plastic deformation requiring time. Typically thermoplastic polymers are used, where, at ordinary imprint temperature, elastic response is quite fast but flow of the molecules requires a reconstruction of the entanglement network. Typical time constants for elastic response are in the range of 1 ms and below, whereas flow time constants may be in the range of several 10 s, depending on the mean length of the polymeric chain. Earlier investigations with polystyrene (PS) showed, that the time-temperature behavior of recovery effects can be well understood on the basis of the time temperature equivalence: recovery effects can be decreased by temperature increase as well as by increase of the imprint time, and the time required for recovery prevention is well correlated with the flow time constants found during rheological characterization<sup>3</sup>.

Elasticity of an entangled polymer is a direct consequence of the entanglement network, which, in contrast to an elastomer, is capable of dynamic rearrangement during flow. This is why we imprinted polymers with shorter chain length, well below the entanglement limit (32 kg/mol for PS). In contrast to the expectations it was found, that even at very low molecular weight (1kg/mol) strong recovery occurred<sup>4</sup>. Obviously the elastic response of a polymer cannot be exclusively ascribed to the entanglement network.

Hence a further processing parameter is currently under inspection, the imprint pressure. It is a matter of fact, that an increase of pressure increases the viscosity and the response time constants of the polymer, as the free volume is reduced. For the zero shear viscosity, temperature dependence and pressure dependence can be described similarly (see Fig. 1), so that an increase of pressure and a reduction of temperature have the same effect.

This is obviously not the case in an imprint, a highly non-uniform and non-linear process. We will show, how a decrease of pressure is effective to avoid recovery (see Fig. 2), even when low imprint temperatures are chosen.

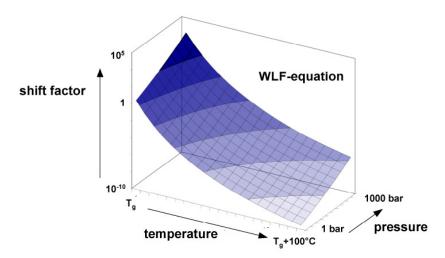
<sup>&</sup>lt;sup>1</sup> L. Ressier at al, Microelectronic Engineering 71 (2004) 272-276

<sup>&</sup>lt;sup>2</sup> G.L.W. Cross et al, Applied Physics letters 86 (2005) 081902-1-3

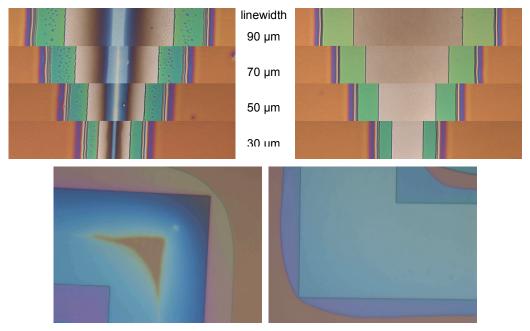
<sup>&</sup>lt;sup>3</sup> H.-C. Scheer et al, J. Vacuum Science and Technology B23 (2005) 2963-2966

<sup>&</sup>lt;sup>4</sup> N. Bogdanski et al, Microelectronic Engineering 85 (2008) 825-829

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*Fig. 1*: Shift factor of zero shear viscosity as a function of temperature and pressure. With increasing pressure and decreasing temperature the polymer flow is reduced. Both dependencies are described here by a WLF-type of equation. An increase of the pressure has the same effect on the zero shear viscosity as a decrease of the temperature.



*Fig. 2*: Results for recovery prevention by adequate pressure control (polystyrene, imprinted layer thickness 200 nm, sample size 2 cm x 2 cm).

Top: low molecular weight (30 k), bottom: high molecular weight (350 k)

Left: imprint at high pressure (100 bar): Strong recovery in the centre of the imprinted structures and e.g. within imprinted corners.

*Right:* imprint at low pressure (10 bar): No recovery, deep imprint.

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