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Microelectronic Engineering 83 (2006) 843–846

MICROELECTRONIC ENGINEERING

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Profile evolution during thermal nanoimprint

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Abstract

The evolution of the profile of an imprinted line under squeeze-flow dominated thermal nanoimprint is investigated experimentally. The results indicate, that in the very first moment the stamp intrusion into the polymer is fast due to shear thinning at the periphery of the feature, proceeding along with the build-up of internal stress in the feature centre. Relaxation of this stress proceeds according to the flow time constants. At processing times that are short compared to the time constants, stress relaxation will not be completed. Then the polymer recovers its initial shape in parts, and this recovery is responsible for the final profile shape. As time constants can be tuned by temperature, these investigations are helpful to define adequate low temperature imprint conditions when mixed pattern sizes are imprinted into spin-coated layers.

Keywords: Thermal nanoimprint; Profile evolution; Time constants; Elastic recovery; Stress relaxation

1. Introduction

During thermal nanoimprint [1] a thermoplastic polymer has to conform to a mould at an elevated temperature under pressure. Typically, thermoplastic polymers feature viscoelastic behaviour, i.e., polymer response depends on the time constants responsible for viscous flow and elastic response of the material at the processing temperature. Therefore, in particular for low temperature NIL (nanoimprint lithography), a subtle tuning of temperature and time is required to result in an accurate imprint for a given range of pattern sizes. Recovery effects may arise, which have been investigated in detail recently [2,3].

Thermoplastic polymers like polystyrene behave according to the well known time–temperature correspondence principle [4]: at different processing temperatures, the imprint proceeds in the same way but at a different time scale. We make use of this principle to experimentally observe the profile evolution during the imprint of elevated stamp patterns. Results with different imprint times in combination with simulations of the elastic effects, which govern polymer behaviour within the first moments of deformation, facilitate the discussion of profile evolution during squeeze-flow dominated thermal nanoimprint.

2. Experimental

We used commercial polystyrene (Sigma Aldrich, $T_g = 95\ ^\circ\mathrm{C}$, $M_w = 350$ kg/mol), referred to as PS 350k, which was characterised [5] before imprinting. From the complex shear modulus master curves the response time constants were derived [6]. At 170 °C, the time constant for elastic response is $\tau_e < 0.1$ ms, the time constant for the onset of flow is $\tau_c = 1.7$ s and the final (longest) flow time constant is $\tau_{0w} = 20$ s.

The imprint experiments were performed in a simple manual press at 100 bar to make use of shear thinning effects [7,8]. Temperature was reduced to 130 and 140 °C to get time constants comparable to well-controllable processing times. Visualization of the imprint process was

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doi:10.1016/j.mee.2006.01.255

realised by conducting a series of imprint experiments where the imprint time was increased from about 10 s to about 25 min, including about 3 s for pressure build-up. After quick cooldown the pressure was released at 70 °C.

In order to ensure crucial squeeze flow conditions with elastic effects, (i) we imprinted into thin layers (130 nm) where macroscopic polymer characterisation may meet its limits, and (ii) we evaluated the imprint of a 40 μm wide isolated line of 500 nm height ($2 \times 2\,\mathrm{cm}^2$ fully patterned stamp). With only two exceptions the results were taken at identical locations.

Elastic behaviour of the polymer was simulated with a commercially available software package (MARC, MSC Software), treating the polymer as a homogeneous, isotropic, continuous, incompressible elastic body according to the classical Mooney–Rivlin equations for the non-linear behaviour of a rubber at high strain [4,9].

3. Results and discussion

For the two processing temperatures the characteristic parameters differ by a factor of 8 [6,7], $\tau_c = 12$ and 1.5 min, $\tau_{0w} = 150$ and 18 min and $\eta_0 = 5 \times 10^7$ and 6.5×10^6 Pa s for 130 and 140 °C, respectively, where η_0 is the zero shear viscosity of the polymers. Elastic response is still below 1 s, so elastic effects are quasi-instantaneous, whereas flow-related effects evolve with time.

Fig. 1 shows profilometer measurements across the 40 μm line for the two processing temperatures. The measurements are levelled with respect to the initial polymer height d_0. With ongoing time the imprint depth increases. The steep polymer wall besides the imprinted line refers to material which has climbed up the stamp [10]. There the stamp cavity is filled in all cases to its full height – stamp height is marked by the shaded rectangle. (The 'overshoots' at the peaks are due to profilometer inertia and potential polymer stretching during separation.) With increasing imprint depth the stamp cavity along the line is filled laterally (see increased width of the peaks).

In accordance with earlier findings [6,8] and in accordance with other groups [2,3] the centre of the imprinted line recovers to its full initial height. Along the line periphery a plastic deformation remains, increasing in width with time. At high enough temperature and/or imprint time the central tip decreases (140 °C, 24 min) and finally vanishes – for 150 °C the imprinted line is flat already after 1 min.

The initial depth and final depth of the imprint, marked as d_i and d_∞, are comparable for the two temperatures. In contrast to other groups [3] we do not assign the difference between d_i and d_∞ to recovery. A steep decrease of the polymer height in the beginning of the imprint and a severe slowdown after short time, as suggested by the profiles of Fig. 1, can be anticipated from calculations in [7].

Simulation of the elastic behaviour shown in Fig. 2 is a further indication. Stress components (a) and strain components (b) are shown when a wide line (only half of it is visible, together with a part of the adjacent cavity) is pressed into an elastomeric layer. The state of deformation (Fig. 2b) indicates, that in the centre of the imprinted line there is some horizontal elongation combined with vertical compression (volume remains constant), but no shear deformation. Towards the periphery of the imprinted line all deformations increase. At the periphery elongation/compression reduces again, but highest shear deformations occur. We believe, that this high shear deformation within very short time ($\sim\tau_e$) gives rise to strong shear thinning and thus to a low local viscosity and efficient outflow of the polymer. As at 140 °C the viscosity is lower than for

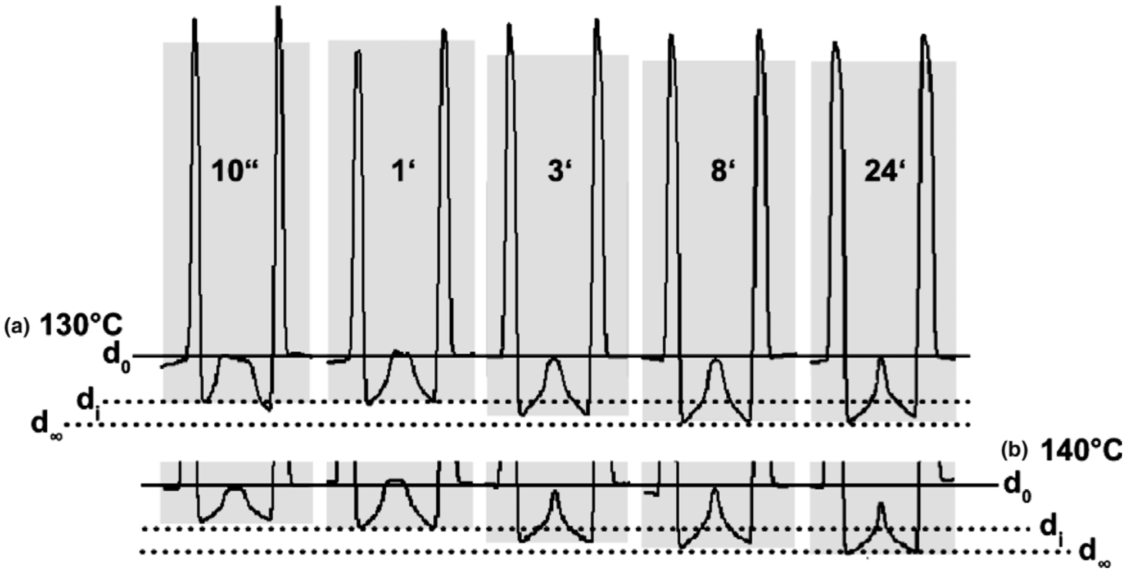

Fig. 1. Profiles (Dektak) across an imprinted 40 μm line (500 nm stamp height, see shading), in a 130 nm polystyrene layer after imprint times of 10 s to 24 min: (a) imprint temperature 130 °C; (b) imprint temperature 140 °C (bottom part of profiles only). d_0 is the initial polymer height, d_i is the initial imprint depth after 10 s, and d_∞ is the final imprint depth after long imprint time.