

2D- visualization of imprint-induced flow by means of crystallizing polymers

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The mechanics governing an imprint process has been investigated in various ways, experimentally as well as theoretically. The efforts range from continuum and molecular dynamics simulations [1] to experimental methods like scatterometry and tracking of marked particles or layers [2]. The present understanding of the forced motion of a thin polymer film from below an elevated stamp structure into the adjacent cavity is summarized in Fig. 1. The polymer is squeezed side-wards, where good adhesion (no-slip) prevails at the substrate interface, whereas a substantial amount of slip has to be expected at the stamp interface due to the use of efficient anti-adhesive layers. In the simple case of full slip at the stamp a maximum lateral velocity (v_x) is expected near the stamp surface but a maximum shear rate (dv_x/dy) near the substrate. Thus a region of high shear rate exists along the substrate interface.

From rheology it is well known that melts of linear polymers (as the typical imprint materials PS or PMMA) disentangle at sufficiently high shear rates, an important factor e.g. during injection molding. Disentanglement is correlated with the orientation of the polymer backbones and thus conformational ordering [3]. Furthermore, it is also well known that organic polymers with conjugated π -electrons along the backbone exhibit strong interaction with polarized light (birefringence). Therefore, when the squeeze-out during imprint results in ordering and when the ordering occurs in a strongly birefringent material [4], optical microscopy should allow a visualization of the flow direction.

In order to proof this idea, we imprinted a highly crystallizing organic polymer, P3HT. Its high tendency towards crystallization is caused by the highly regular chemical structure (high 2-5 HT coupling, regio-‘regular’ P3HT), leading to anisotropic optical properties. In contrast, regio-‘random’ P3HT (low 2-5 HT coupling) features less order and behaves isotropically. Fig. 2 compares the imprint of random and regular material. The regular material clearly shows an anisotropy correlating with the squeeze direction, whereas the random material does not. Fig. 3 documents the situation under detection at different rotation angles of the polarizer. We take the locally differing intensity with rotation as an indication of birefringence and thus of flow-induced orientation. To further prove the assumptions, the imprinted patterns were investigated via SEM and WLI (Fig. 4): The surface is flat, indicating optical anisotropy, only.

We will show results for different layer thicknesses and imprint temperatures for organic polymers with crystallization tendency and discuss the benefit of such experiments for 2D flow visualization in imprint. Beyond that such investigations are useful to clarify the crystalline structure of such materials [5].

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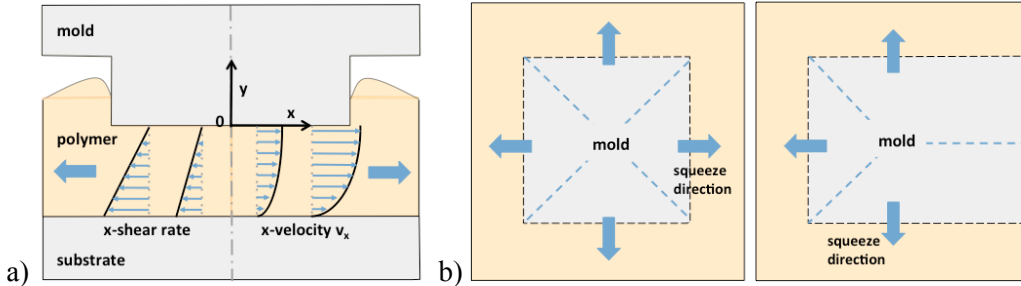
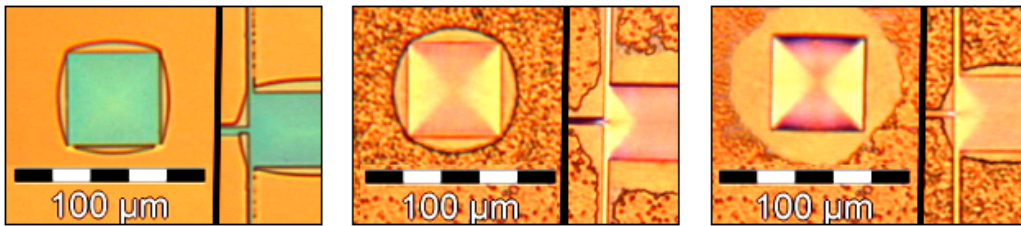


Fig. 1. Conceptual sketch of the squeeze-out of polymer underneath an elevated stamp structure during imprint, a) side view and b) top views. The lateral velocities and shear rates are indicated in the right and left part of a), respectively.



(a) 'Random' P3HT, 80°C (b) 'Regular' P3HT, 180°C (c) 'Regular' P3HT, 200°C

Fig. 2: Structures imprinted in P3HT (thickness ≈ 300 nm, imprint 4 min, 100 bar). Only the regular material shows anisotropy (cross in square pad, triangle at line end).

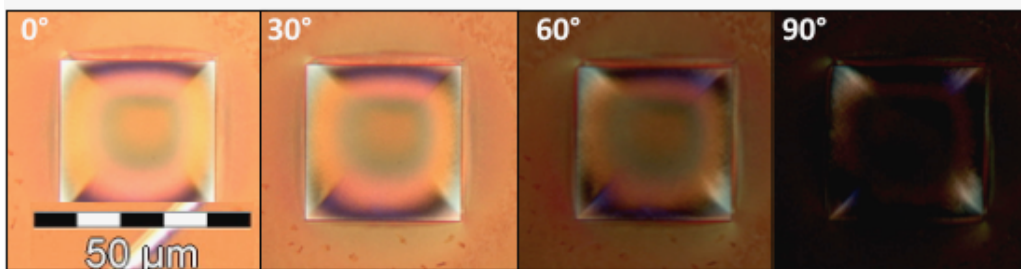


Fig. 3: Optical micrographs of square pads under detection at different rotation angles of the polarizer (regular P3HT, imprint at 200°C, 4 min, 100 bar).

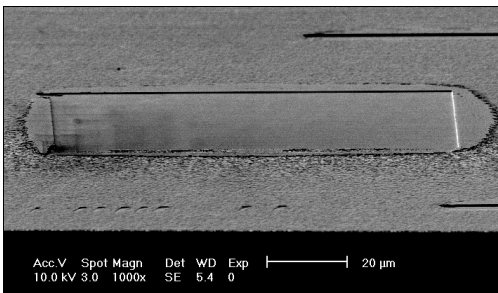


Fig. 4: SEM micrograph of the imprinted square pad of Fig. 3.

Underneath the elevated stamp structure the surface of the polymer is flat. This was also proven by white light interferometry (WLI). Thus the colors in Fig.3 originate from an anisotropy of the refractive index.