

Contact angles in a thermal imprint process

Nicolas Bogdanski*, Matthias Wissen, Saskia Möllenbeck, Hella-Christin Scheer
University of Wuppertal, Rainer-Gruenter Str. 21, D-42119 Wuppertal, Germany

Every imprint process is governed by material flow, where the material properties, the polymer as well as the surface properties of the stamp and the substrate, determine the flow characteristics. In a typical flow situation the contact angle between the polymer and the stamp on the one hand and between the polymer and the substrate on the other hand are of paramount importance since they decide about wetting or non-wetting of the polymer on the respective surface¹. For thermal imprint, in contrast to other imprint techniques, wetting is not vital. The high imprint forces ensure filling of the stamp cavities. Nevertheless, even for thermal imprint the implementation of contact angles is important for correct imprint processes simulation². In addition, the appearance of filling defects suggests the consideration of contact angles in order to understand the phenomena observed.

Contact angles are easily accessible, they can simply be calculated by well known equations³ through surface energies, γ , of the involved materials that can either be found in literature or can be measured. The contact angles displayed in Tab. 1 are calculated for the substrate-polymer and the stamp-polymer interface at ambient conditions. The surface-energy γ is assumed to adopt values measured elsewhere⁴ for the stamp coated with an anti-sticking-layer (ASL). Tab. 1 shows that the calculated contact angles indicate complete wetting of the polymer on the substrate, the contact angle is 0° , and partial wetting of the polymer on the stamp, the contact angle is 84° .

Fig. 1 shows the micrographs of an imprinted PMMA layer. As the initial layer was reduced to incompletely fill the stamp's cavities and a relatively high imprint temperature enabled sufficiently low viscosities, contact angles could be observed after the imprint. Dashed lines (Fig. 1 right) mark the relevant contact angles, which strongly differ from the calculated ones. Nonetheless in accordance with Tab. 1, the contact angle between the polymer and the substrate (1) is smaller than the one between the polymer and the stamp (2).

Within our approach we will give possible reasons for the difference between calculated contact angles and those measured at imprints. Due to thermal expansion of the material, the surface energy is temperature dependent, it decreases with increasing temperature. Fig. 2 gives the example of the temperature dependence of γ for PMMA that is strongly related to the temperature dependence of the polymer's specific volume. Hence γ features a step of the gradient as it passes the glass transition. Further we will discuss (a) to what extent measured contact angles do reflect the polymer in its equilibrium state and (b) how far potential polar fractions of γ play a role. However, there is a need to evaluate whether contact angle optimization is efficient for imprint defect prevention.

¹ P.-G. de Gennes et al, *Capillarity and wetting phenomena*, Springer (2004)

² J.-H. Jeong et al, *Fibers and Polymers* **3**, (2002) pp. 113-119

³ D.W. van Krevelen, *Properties of polymers*, Elsevier (1990)

⁴ S. Park et al, *Microelectronic Engineering* **73-74**, (2004) pp. 196-201

* email: bogdanski@uni-wuppertal.de

	Si substrate: SiO ₂	Si stamp: ASL
PMMA	0°*	84°

Tab. 1: Contact angle of PMMA on the silicon substrate (native oxide on the substrate surface) and PMMA on the anti-sticking-layer (ASL) as calculated by commonly used equations at ambient conditions. (*Due the fact that PMMA completely wets the substrate surface no value for θ can be calculated. The value of 0° therefore reflects complete wetting.)

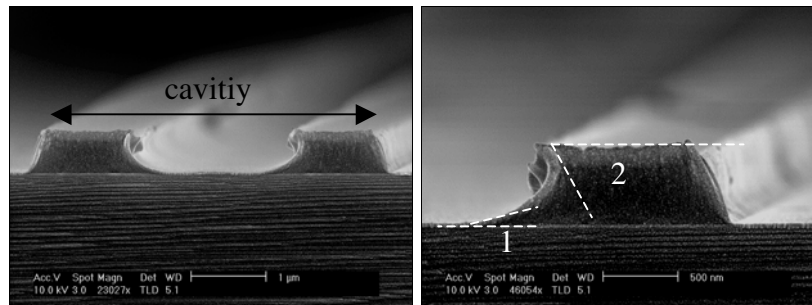


Fig. 1: Imprint into PMMA at 230°C. In order to identify contact angles, the cavities were not filled completely. Left: 5 μm wide cavity (500 nm high). The incomplete filling causes a symmetric ‘non-filled’ region in the middle of the cavity, whose shape is determined by the respective contact angles. Right: Close up micrograph, highlighting the contact angles at the substrate-polymer interface (1) and at the stamp-polymer interface (2).

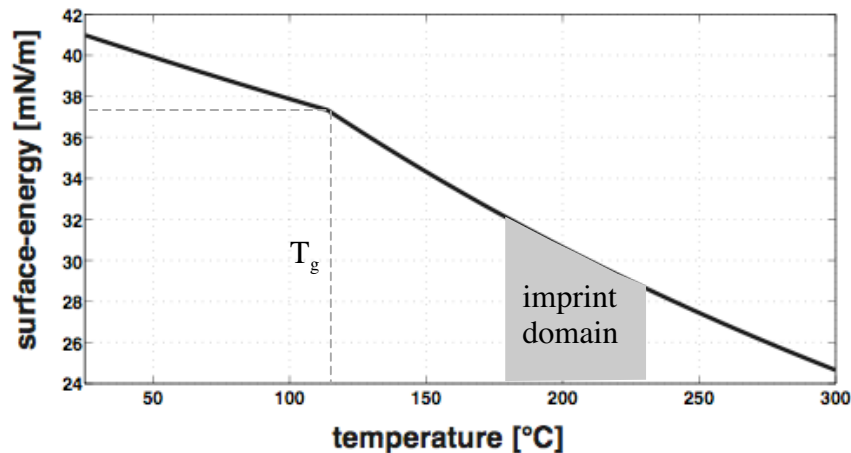


Fig. 2: Temperature dependence of the surface energy of PMMA. At room temperature, γ equals 41 mN/m³. Within the glass transition γ is below 40 mN/m. There, a step of the gradient occurs which is related to the polymer specific temperature-volume dependency. Within the domain where PMMA is usually imprinted γ can be smaller than 30 mN/m.