

The impact of glass temperature for thermal nanoimprint

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It is well known that the glass temperature T_g of a polymer is not a doubtless parameter for use as an estimate to determine an adequate imprint temperature during thermal nanoimprint (T-NIL) of polymers of mean molecular weight. Measured values depend on the cooling rate¹ and thus polymer history. They denote the temperature position of a transition region, where the width may be polymer specific. Often T_g values for commercial polymers provided by the manufacturers differ from the values reported in the literature. This may be due to the fact that commercial polymers are blended with additives to improve their quality for a certain application, which may be far from micro- or nanotechnology. In addition, very thin layers of polymer (100 nm and below) may not be adequately described by a bulk T_g ², as for these thin layers the interaction with rigid boundaries (substrate, elevated stamp areas) on the one hand and/or the interaction with the free surface (stamp cavities) dominate the behaviour, so that it is hardly possible to define such a global parameter like T_g for thin polymer layers.

Despite these peculiarities the glass temperature often serves as an indicator to define an adequate imprint temperature for a thermal NIL process. In order to address the practicability of such an approach we have chosen three different 'classical' polymers, (poly)styrene (PS), (poly)methylmethacrylate (PMMA) and (poly)vinylchloride (PVC), so that knowledge from literature may be adopted to interpret the imprint results. For the PS also characterisation measurements are available³. Respective data of the three polymers are listed in Table 1. The molecular weights were chosen in the medium range, 220 kg/mol to 350 kg/mol. So the imprint behaviour of the three materials should be comparable when imprinted at comparable levels above their respective T_g .

Our results clearly show, that this is not the case (see examples in Fig. 1). The imprints were performed into layers of 200 nm thickness under partial cavity filling, so that imprint depth and thus flow boundary width can easily be interpreted in terms of viscosity. In contrast to the respective T_g values, PS features the lowest viscosity under comparable conditions, whereas PVC features the highest one. In particular we will report on pattern size dependence of the observed discrepancies.

¹ R. Schwarzl, *Polymermechanik*, Springer (1990); D.W. v. Krevelen, *Properties of Polymers*, Elsevier (1990)

² K. Dalnoki-Verres et al, *Phys. Rev. E* 63, 63 (2001); C.-J. Ellison et al, *Nature Materials* 2, 695 (2003); S. Sills et al, *J. Chem. Phys.* 120, 5334 (2004); G. Reiter, *Eur. Phys. J. E* 8, 251 (2002)

³ H. Schulz et al, *Microelectronic Engineering* 78-79, 625 (2005)

| | PMMA | PS | PVC |
|--|---------|---------|-------|
| T_g (supplier) / °C | 110 | 95 | – |
| T_g (literature ¹) / °C | 105-110 | 95 | 70-80 |
| M_w (supplier) / kg/mol | 350 | 350 | 220 |
| M_w (measurement ³) / kg/mol | – | 235-278 | – |

Table 1: Data set for the investigated polymers

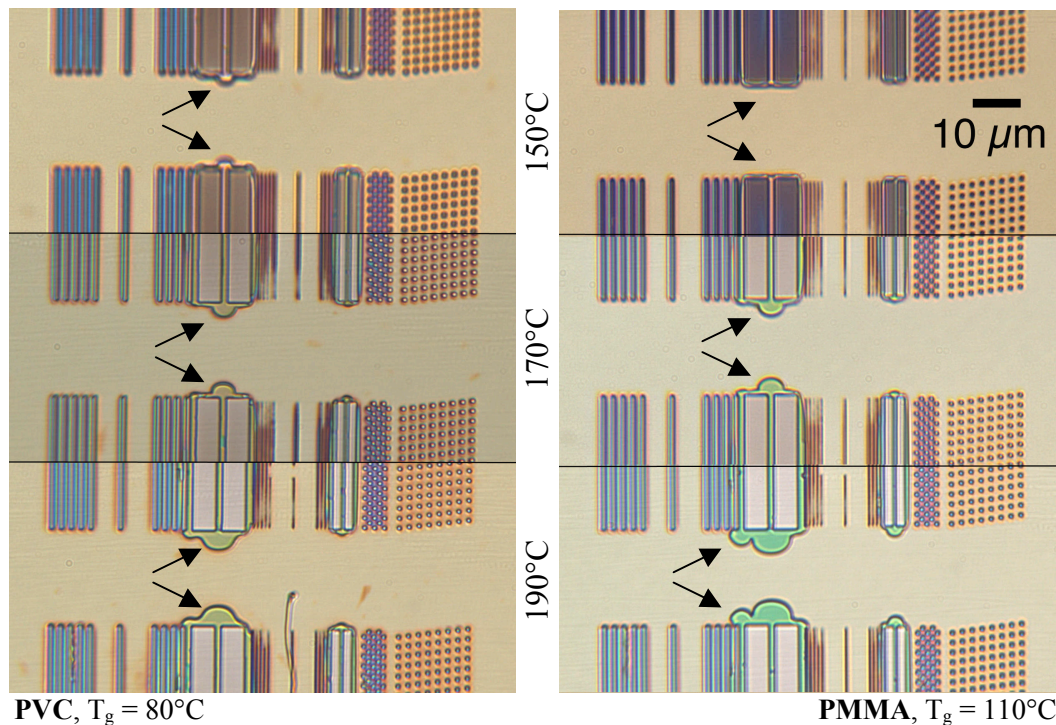


Fig. 1: Comparison of flow properties of the polymer with the lowest T_g , PVC (left) with the flow properties of the polymer with the highest T_g (PMMA) under investigation. Three different imprint temperatures are documented, 150°C, 170°C and 190°C. The pictures show test structures (isolated/nested lines and dots, positive and negative), pattern sizes are from 400 nm to 1 μ m.

The imprint depth and thus the effective viscosity of the polymer can be estimated by considering the width of the flow boundaries around the structures (marked).

At 150°C, PVC shows lower viscosity than PMMA, however not corresponding to the glass temperature difference of about 30°C. At high temperature (190°C) PMMA shows even lower viscosity than PVC. Lowest viscosities are found during imprint of PS under the same conditions (not shown here).

For larger pattern sizes the behaviour of the three polymers is apparently different.