

Pulsed Force Mode™ Applications

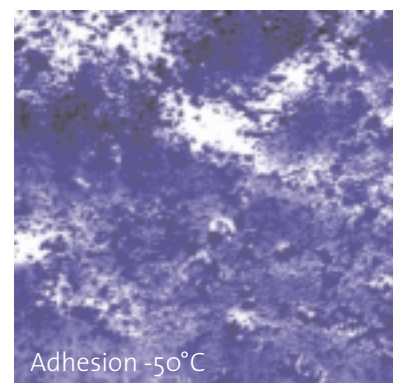
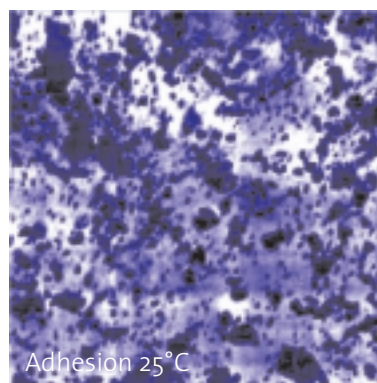
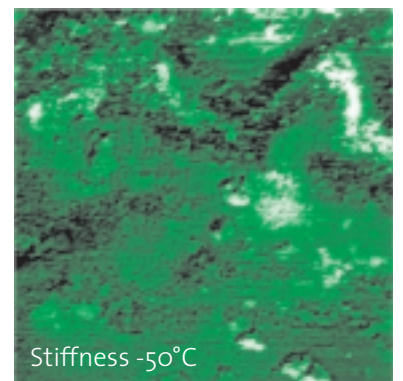
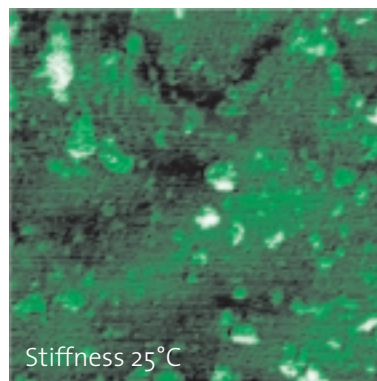
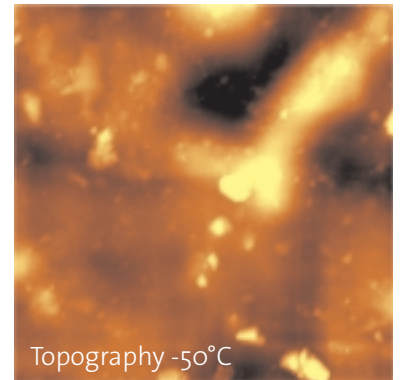
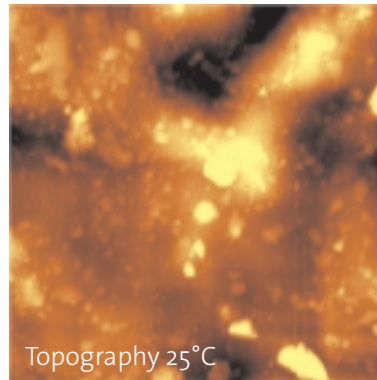
Segmented Polyurethanes

In this study, elastomeric segmented polyurethane (SPU) samples were investigated. Numerous studies have been published on the morphology of such materials to characterize their phase-separated structure. These typically reveal domain sizes on the order of 5-25 nm. The aims of the current study were: (1) to investigate the effects of the glass transition on Pulsed Force Mode (PFM) results for a model system and determine whether the behaviour can be used to elucidate structure and identify phases. (2) To investigate the ability of variable-temperature PFM to characterize phase-separated segmented polyurethane elastomers.

The figure shows images obtained at room temperature (left column and -50°C (right column) for SPU incorporating the 1,3-dihydroxybenzene chain extender. Scan range 10 x 10 μm (topography top, stiffness images middle, and adhesion images bottom). Dark areas indicate low values in each case.

The topographic images confirm that the same area was scanned at the two temperatures and that changes in topography are not responsible for the changes in the other images. Excellent contrast is apparent in the room temperature adhesion image. A high concentration of occluded domains or phases is revealed, with relatively low surface adhesion, embedded in a relatively high-adhesion continuous phase. The domains range in diameter from under 100 nm to over 400 nm (text continued on the following page).

This work was carried out by D.B. Grandy, D.M. Price and M. Reading, University of Loughborough, UK.

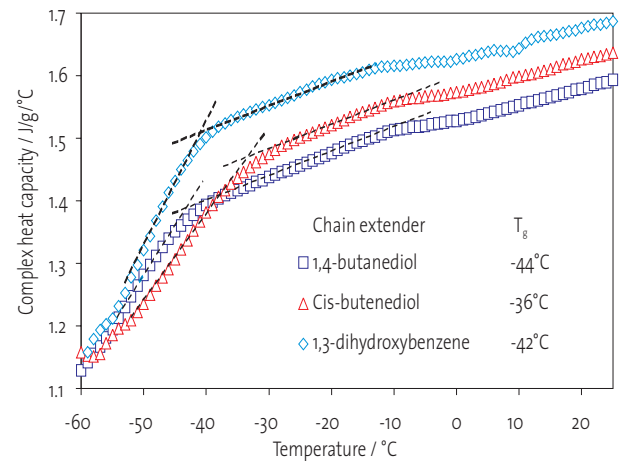


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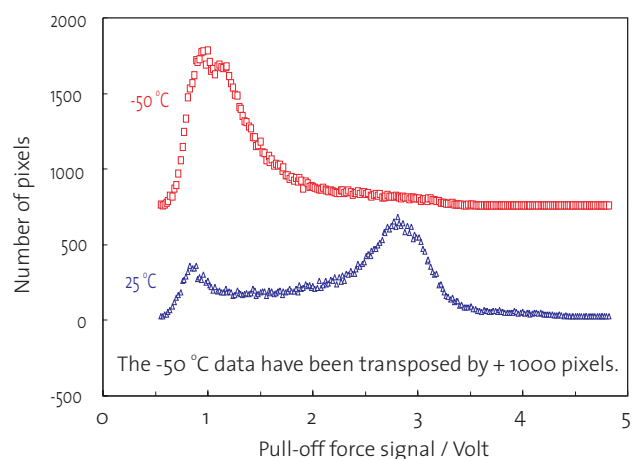
Segmented Polyurethanes

This morphology is also reflected in the local stiffness image, although with less contrast and detail (this sample provided the best indentation images encountered in the study). The low adhesion phases must, therefore, be relatively stiff or hard structures. These presumably incorporate predominantly hard segment material, in the surface layer at least. Their size, however, is at least an order of magnitude greater than that expected for individual hard-segment domains in this type of SPU. As far as the authors are aware, this is the first time that such high-contrast 'real space' images have been obtained using a thermally-based technique, which show clearly the phase-separated microstructure of a SPU at a scale substantially larger than that of individual domains. At -50°C , the contrast all but disappears, because the continuous phase is now much less adhesive towards the tip. There is, however, still a region towards the top of the image with relatively high pull-off force, which is associated with the highest areas shown in the corresponding topographic image. The cause of the high adhesion is, therefore, almost certainly that this region had not yet fully cooled below the T_g of the soft segment material. The indentation force image still suggests that the occluded domains are marginally stiffer than the surrounding material.

The modulated temperature differential scanning calorimetry (M-TDSC) results in the figure show that, on heating, this material undergoes a glass transition that finishes at approximately -42°C . This is the only transition between -50°C and room temperature and occurs in the soft segments of the polyurethane chains. This result, combined with the images at above and below the onset of the glass transition, therefore serves to identify the phase with high adhesion at room temperature as being soft segment-rich. In this case, and all others in this study, at the lower temperature of -50°C , the soft segment is not beneath the onset of its glass transition, but is partially into it as measured by M-TDSC. However, the M-TDSC measurement was carried out at 0.025 Hz , whereas the PFM measurements were made at 500 Hz . This difference in frequency will tend to make the glass transition, as seen by PFM, significantly higher than that detected by M-TDSC. This should, therefore, enhance our ability to detect the effect of the transition on PFM measurements. The occluded hard domains are shown in the topographical images to be higher than the surrounding continuous phase. The line measurement selected from the room temperature image shows that they range in height from approximately 20 nm to 150 nm above the average level of the continuous phase. Some topographical contrast is lost at -50°C . A possible explanation is that the, now glassy, soft segment material is no longer deformed to the same extent by the compressive stresses imparted by the tip during the indentation part of the measurement cycle. This would be consistent with the stiffness images.



Looking at the histograms of the adhesion images in figure at the right, we see a virtually mono-modal distribution at low temperatures changing to a well-differentiated bimodal distribution at room temperature. The material that has formed the higher pull-off force peak at room temperature is presumably the material that has passed through its glass transition. This corresponds to the continuous phase. This behaviour echoes that seen for PS-PMMA blends, except the differentiation between the two phases at higher temperatures is even more marked.



For more details see "Micro-thermal characterization of segmented polyurethane elastomers and a polystyrene-poly(methyl methacrylate) polymer blend using variable-temperature pulsed force mode atomic force microscopy" by D.B. Grandy, D.J. Hourston, D.M. Price, M. Reading, G.G.Silva, M. Song and P.A. Sykes accepted for publication in *Macromolecules*.