Surface enrichment layers in pressure sensitive adhesive films

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Pressure sensitive adhesives (PSAs) are used for many different applications, such as for example adhesive foils or binding materials. A prominent class of PSA films is based on statistical copolymers. Typically two or three different monomers are combined into the statistical copolymer to balance the different requests of the PSA [1-4]. The adhesive properties of the PSA films are mainly determined by surface-near regions. However, detailed information about surface structures of such adhesive films is still missing.

In the presented work we focus on PSA model systems of statistical copolymers consisting of two different types of monomers. In one series of samples the polymer chains are composed of 80% poly(butyl acrylate) (PBA) and 20% poly(methyl acrylate) (PMA) with different molecular weights. A second type of statistical copolymer, which is denoted with P(EHA-stat-MAA), uses 90% poly(ethyl hexylacrylate) (PEHA) and 10% poly(maleic acid anhydride) (PMAA). It has a molecular weight of 187k and a sample age of seven days.

The PSA films were prepared with solution casting on pre-cleaned glass substrates. From a naive point of view, one would have expected homogenous films, which are characterized by the average monomer composition. To investigate the surface structure, we probed the refractive index profile (which is equivalent to a composition profile) perpendicular to the PSA surface using x-ray reflectivity (XRR) for the molecular weight series. For P(EHA-stat-MAA) we performed grazing incidence small angle x-ray scattering (GISAXS) measurements to prove the existence of lateral structures.

![X-ray reflectivity data and fits of the statistical copolymer with 80% BA and 20% MA and a molecular weight of a) 60k, b) 200k and c) 600k and the resulting refractive index profiles.](image)

The figures 1a, b and c show reflectivity curves in a typical representation, which is beneficial for thin enrichment layers. The curves plotted in green color represent freshly prepared samples (see
sample age within the respective figures) and the curves plotted in blue color show data from samples which were stored for more than twenty days under room temperature conditions. The red solid lines are the fits to the data performed with Parratt32. The figures 1d, e and f show the corresponding refractive index profiles where z = 0 denotes the sample surface. The black solid lines are positioned at the values of the refractive indices of the corresponding homopolymers related to the involved copolymers. For higher molecular weights (figures 1e and f) freshly prepared samples show no or only a little surface enrichment of the PMA component. During aging the PMA content near the surface is increased in such a way that the surface is dominated by the PMA component. For the low molecular weight sample (figure 1d) the PMA component is enriched at the surface even for the freshly prepared sample. The reorganization process at low molecular weight is much faster than for high molecular weight samples. In any case this is a surface effect. For a depth z > 100 nm the average monomer composition is reached, which is 80:20 for the investigated system.

The GISAXS measurements (wavelength of 1.38 Å and beamsize of 40 μm x 20 μm) were performed at the beamline BW4 at HASYLAB. The incident angle on the sample surface was selected to 0.506° and the distance between the sample and the detector was 2.004 m. A 2D-MarCCD detector (2048 x 2048 pixels with a pixel size of 79 μm) was used to record the scattered x-rays from the film surface. The so called out-of-plane cut through the 2D-scattering pattern is selected in order to look for the evidence of lateral structures. It is oriented parallel to the sample surface and perpendicular to the beam direction (along y-axis, see red line in figure 2a). The out-of-plane cut is made at the critical angle of PEHA.

![Figure 2: a) measured and b) simulated 2D GISAXS pattern of P(EHA-stat-MAA), c) out-of-plane cut at the position of the critical angle of PEHA (red circles) and corresponding fit (black solid line).](image)

The out-of-plane cut (figure 2c) clearly shows a shoulder which indicates the presence of a lateral structure. For analysis the data are simulated with the IsGISAXS software. A model which assumes cylinders of increased refractive index and thus a different monomer composition close to the sample surface turned out to be appropriate to fit the complete 2D scattering patterns (compare for example figures 2a and b). For the particular example shown in figure 2, the cylinders have a mean diameter of 18 nm and a mean distance of 83 nm. Due to the broad distribution of both characteristic lengths no Bragg-like peak is detected.

References