Adhesives

Pressure sensitive adhesives (PSAs) stick to a huge variety of materials by applying a slight pressure. Based on polymer compositions, the rheological properties of PSAs play a key role in the phenomenological appearance of tackiness. From the mechanical point of view, a PSA possesses a visco-elastic nature. At long time scales the viscous aspect dominates and enables the adhesive to achieve an intimate contact to the surface of a solid specimen, adapting to the latter surface profile. On the other hand the elastic properties, mainly gaining in importance at short time scales, allow the adhesive to sustain short time shear forces. The fact that PSA combine both aspects at the same time distinguishes them from other types of adhesives stepping from a fluid state to a solid state by for example a change in temperature or through a chemical reaction. The lack of hardening enables in PSA application a desired, controlled release of the adhesive bond. One of the most prominent examples in daily life are stick-on notes, in addition making use of the ability to undergo several cycles of bonding and detaching. Scientifically, the quality of adhesion can be quantified in the so-called tack test (figure 1). A probe punch, like a flat-ended rigid cylinder, is pressed with a defined force onto a PSA film. After maintaining the force for a well-defined time the punch is withdrawn from the surface with a fixed velocity. During the whole process the force needed to sustain the constant retraction velocity is probed as function of the distance between film and punch. Usually, the resulting curves show characteristic features such as a sharp maximum followed by an extended force plateau. Even up to film-punch distances of multiple film thickness a non-zero force value is detected. The geometry of the tack test with a flat ended cylinder ensures, contrary to a comparative test with a spherical indenter, a uniform spacing of substrate and punch. Despite the homogeneous elongation throughout the contact area a highly heterogeneous structure of cavities and fibrils develops in the polymer. In other words, the material has to face the challenge to occupy a rapidly increasing volume and to respect its low compressibility as well. The debonding process during the tack test is analyzed in detail by optical microscopy from both underneath, through a transparent substrate, and from the side.

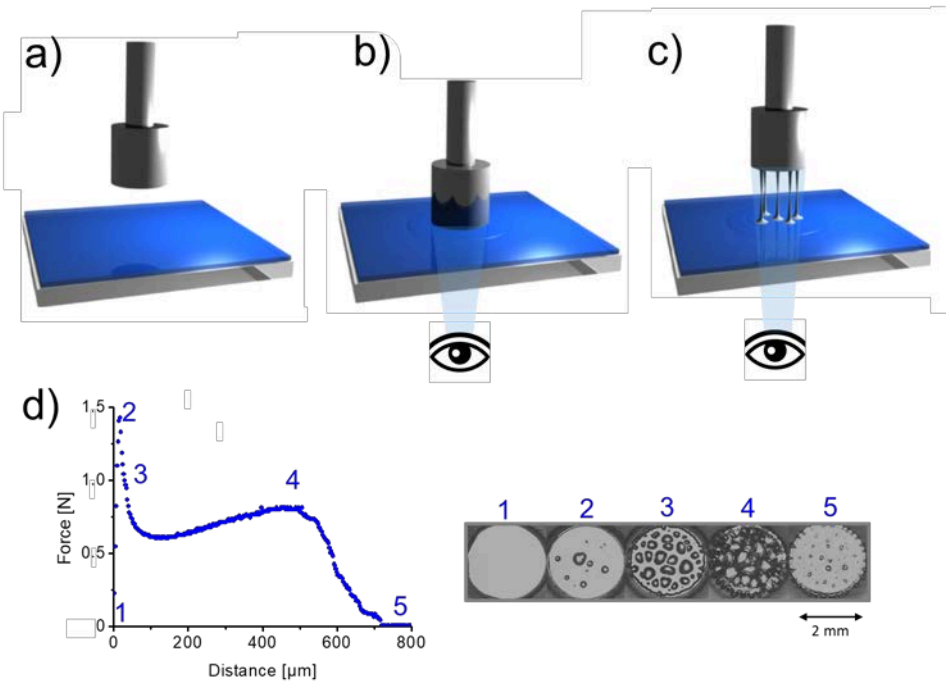

Figure 1: Schematic of the tack test: a) approach of flat-ended cylinder with defined velocity b) maintaining a defined force for a certain time c) retraction of the cylinder with fixed velocity;

observation of the debonding from underneath through a transparent substrate with optical microscopy d) exemplary force-distance curve and optical microscopy for a PSA based on a triblock copolymer.

In order to improve the tack of polymers which are used as adhesives, the mechanisms of bond formation and separation have to be understood. Different characteristic stages of adhesive failure can be discovered by the means of optical techniques (see figure 1d). Firstly the polymer film is elongated homogeneously in the direction of tension accompanied by a sharp increase of the force. As traction proceeds cavities are introduced into the film locally. Accompanied with a stress release the appearance of cavities corresponds to the force maximum. As the cavities expand laterally, the force promoting debonding suddenly decays to a comparatively low, but non-zero value. A plateau of constant or moderately increasing height in the force versus distance curve follows and the cavities already occupying most of the nominal contact area now expand mainly vertically. As the cavities remain well separated the polymeric material in between still provides a local connection between the punch and the substrate. With proceeding debonding the film transforms out of a foam like state to a fibrillar structure. Finally when air rushed in from the outer border of the vertically expanded film the measured force vanishes to zero. Thanks to investigations of PSA failure by optical microscopy a detailed understanding of the highly non-linear force-distance curve in the test has been obtained. Nevertheless all experiments are restricted towards small length scales by the optical resolution limit. In order to overcome this limit we apply scattering techniques.

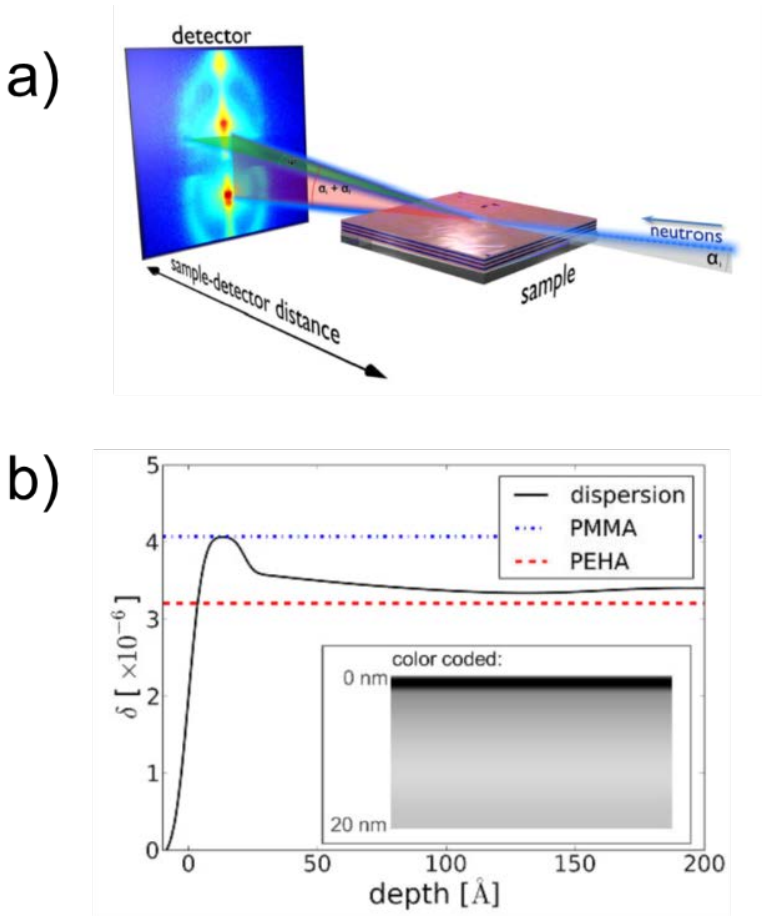

Figure 2: Morphology investigations of adhesive films with neutrons: a) Scheme of grazing incidence small angle neutron scattering (GISANS) addressing lateral structures b) Near-surface region of a model adhesive of a statistical copolymer. From the dispersion profile obtained with neutron reflectivity measurement PMMA enrichment of statistical copolymer at the surface (black color coded in the inset) is proven.

We combined the mechanical test with x-ray scattering experiment in transmission. With USAXS experiments the fibrils created during the debonding are observable. Using a reflection geometry, grazing incidence small angle scattering (figure 2a shows the scheme of GISAS with neutrons) gives access to a statistical description of the related surface morphologies. With GISAXS we were able to identify lateral structures for ultrathin adhesive layers of a model adhesive of a statistical copolymer. With neutrons in a time-of-flight mode (TOF-GISANS) it is moreover possible to obtain depth-resolved structural information. For an acrylic statistical copolymer we found that at the buried interface of adhesive and adherent lateral structures are absent whereas at the surface small and rare defects around 40 nm are present. For the bulk volume of the film even smaller structures were resolved.

Most PSAs are multicomponent systems or at least consist of different structural units if it constitutes a copolymer. For the understanding of an adhesive it is important to gain knowledge about the inner composition and possible enrichment of components at the surface and at the adhesive – adherent interface. Furthermore for applications it is of major importance how this might change under certain ambient conditions e.g. high humidity. Insights in the profile of the composition can be gained by reflectivity measurements with x-rays and neutrons, respectively. For an acrylic statistical copolymer we investigated the near-surface composition of adhesive films stored at different relative humidity from 2 to 96% with XRR and correlated the results with tack measurements under corresponding humidity conditions. An example for the enrichment of one component of a statistical copolymer at the surface with neutron reflectivity is given in figure 2b. Neutron reflectometry also allows for investigations in situ. During the drying process out of deuterated toluene solution the near-surface solvent concentration profile could be monitored with time. We found that with increasing molecular weight the maximum evaporation velocity decreases and the equilibrium stage is reached at later times. Also it could be proven that independent of molecular weight of the polymer a very small amount of solvent remains.

With our utilization of scattering methods we introduced a new experimental range into the scientific area of PSAs. Our interest is the combination of these scattering methods with established mechanical tests. We extend our view to more complex geometries and adhesive joints like curved surfaces as given for fibers as well as medical sensors and wearable devices in direct contact with the skin.

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