Microscopic structure in pressure sensitive adhesives: an ultrasmall angle X-ray study

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Abstract

We applied ultrasmall angle X-ray scattering (USAX) in the context of pressure sensitive adhesive (PSA) debonding. Microscopic structures, as detected by USAX, complete macroscopic structural information from standard optical microscopy. As a model PSA, a statistical copolymer was investigated. Asymmetric USAX pattern were detected. The data are modelled by a tilted one-dimensional grating of slits.

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1. Introduction

Pressure sensitive adhesives (PSA) are based on polymers. They adhere by simply applying pressure to a huge variety of materials. In many PSA applications, a controlled release of the adhesive bond is desired. One of the most prominent examples in daily life is stick-on notes, making use of the ability to undergo several cycles of bonding and detaching. Scientifically, the quality of adhesion is quantified in the so-called tack test [1]. A probe punch, like a flat-ended cylinder, is pressed with a defined force on to a PSA film. After maintaining the force for a controlled time, the punch is withdrawn from the surface with a fixed velocity. During the process, the force needed to sustain the constant retraction velocity is probed as a function of the film–punch distance. Usually, the resulting curves show characteristic features such as a maximum force followed by a force plateau. Even at film–punch distances of multiple film thicknesses, the formerly glued interfaces remain locally connected by a fibrillar structure. PSA debonding during the tack test was analyzed in detail by optical microscopy from both underneath, through a transparent substrate, and from the side [2]. In early debonding stages

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macroscopic cavities appear locally, introduced into the former homogenous film by hydrodynamic stress. With proceeding tension, they grow in number and size until the former contact area is almost completely covered (see Fig. 1a) [3,4]. Finally, the polymeric material located at the cross-over point of walls separating cavities is elongated in direction of tension. Thereby numerous fibrils are formed. Nevertheless, investigations by conventional microscopy are restricted towards small length scales by the optical resolution limit. In order to overcome this limit, we applied in situ ultrasmall angle X-ray scattering (USAX) during the tack test [5].

As a PSA model system, we investigated a statistical copolymer of 80% 2-ethyl hexylacrylate (EHA) and 20% methyl methacrylate (MMA). PSA films were prepared on top of float glass slides, which had been pre-cleaned in an acid bath [7]. The polymer was dissolved in iso-butanol with a concentration of 70 g/l. By solution casting on well horizontally placed slides, films of approximately 30 μm thickness were prepared. In the tack test, a glass cylinder with 2 mm diameter was pressed on to the film with a force of 6 N. After 10 s, the punch was retracted from the film with a velocity of 1050 μm/s. During the mechanical test,

a fibrillar structure developed which was investigated by in situ USAX. The experiments were performed at the beamline BW4, HASYLAB (Hamburg).

In transmission geometry, the scattered intensity was recorded with a 2D detector. The direct beam, which had a diameter of approximately 400 μm, was shadowed by a beam stop. At a wavelength of 0.14 nm and a sample detector distance of 13.2 m, structures between 25 and 400 nm were resolvable. The PSA film was placed parallel to the incident beam shadowing only a small part of the beam. While the film and the beam remained solidly attached, the punch was retracted in the direction perpendicular to both film surface and incoming beam (see Fig. 1b). At several film–punch distances scattering patterns were recorded. To clarify further geometrical considerations, we define the x-axis as the direction of the incident beam. The film was thus located in the (xy)-plane whereas traction in the tack test was directed along the z-axis.

The resulting scattering pattern contain, besides the USAX signal, diffuse scattering from the PSA surface. Focussing on the USAX signal, we restrict ourselves to horizontal cuts out of the 2D intensity map through the direct beam position and parallel
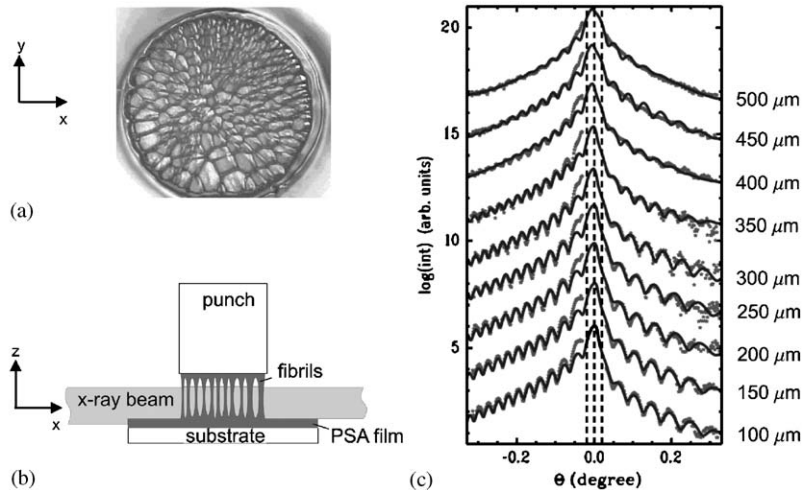

Fig. 1. (a) Optical microscope image of the fibril forming process, taken from underneath through a transparent substrate. (b) Schematic side view of in situ USAX at the fibrillar structure resulting from the tack test. (c) Horizontal cuts from the 2D scattering pattern for several film–punch distances. The logarithmic intensity is plotted versus the scattering angle. For clarity, the curves are shifted along the intensity axis. Solid lines refer to the fit, whereas dashed lines mark the resolution limit.

to the PSA film surface ($q_z = 0$). In Fig. 1c, the resulting curves are displayed for several film–punch distances. The cuts show well-pronounced multiple fringes. With increasing distance the amplitude of the modulation in intensity decays. A further eye-catching feature is the strong asymmetry of the curves with respect to the scattering angle. Both intensity and angular positions of the fringes depend on the sign of the scattering angle. In the following, we will refer to the latter aspect as positional asymmetry. The degree of asymmetry in intensity is smaller for those curves with less pronounced fringes. In order to quantify the positional asymmetry, the minima in intensity were numbered by the index j and plotted versus the corresponding scattering angle θ. Negative numbers correspond to negative scattering angles. A parabolic correlation is observed which is exemplarily shown in Fig. 2a for the scattering curve measured at a film–punch distance of $100\,\mu m$. The asymmetry prevents standard evaluation and plotting of the scattering data. In the first Born approximation, the measured intensity is given by the absolute square of the spatial Fourier transform of the electronic density. Thus intensity is, being independent from the detailed electron distribution, an even function of momentum transfer. As we restrict to momentum transfers with no vertical component ($q_z = 0$) with respect to the film surface, in the first Born approximation asymmetry can only be introduced by the curvature of the Ewald sphere. Nevertheless this is a minor effect in USAX.

One simple model to explain positional asymmetry is scattering at a one-dimensional grating of

small slits tilted in the (xy)-plane. Geometrically this means that each slit, displayed with respect to the neighboring one by D_{y0} in y, is in addition shifted by D_x in beam direction (see Fig. 2b). Basic geometrical considerations on the path difference Δs in between neighboring slits lead, in small angle approximation, to a parabolic correlation of the index j to the corresponding scattering angle θ;

$$j(\theta) = \frac{n}{\lambda}\left(D_{y0}\theta + \frac{D_x}{2}\theta^2\right). \tag{1}$$

n refers to the total number of slits and λ is the wavelength. Inversion symmetry in $j(\theta)$ is broken by $D_x\theta^2$. The ratio $\eta = D_x/2D_{y0}$ can thus be considered as a parameter governing the degree of positional asymmetry. In detail $42 < \eta < 50$ holds for all scattering curves in Fig. 1c. The total number of slits n cannot be determined by the fit. Nevertheless, a lower limit can be extracted from the number of side minima i (fringes). As 11 minima have been observed at one side in the scattering curves, n has to exceed $2i = 22$. For all film–punch distances the relation $210\,nm < nD_{y0} < 257\,nm$ is valid. In the context of adhesive debonding, the slits might be embodied by elongated micro-bubbles embedded in the polymeric fibrils [5]. The existence of micro-bubbles was proposed in theory [6]. Referring to the image of micro-bubbles, the constant value of nD_{y0} with respect to the film–punch distance states that the region containing micro-bubbles in the fibril remains to be of constant lateral extension during traction. The very existence of micro-bubbles as a substructure of adhesive fibrils shows that structure creation, well-known at macroscopic length scales, is also proceeded in the range of nanometers.

Based on the quantitative description of positional asymmetry, a model was developed in order to fit the scattering data:

$$I(\theta) = N_{L/R}\iint dD_y\, d(\theta_1)\, e^{-\sigma^2\theta_1^2}$$

$$\times f(D_y)B(\theta - \theta_1)\left(\frac{\sin(\pi j(\theta_1))}{\sin(\pi j(\theta_1)/n)}\right)^2. \tag{2}$$

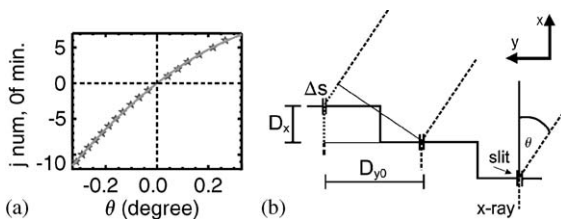$f(D_y)$ represents a Gaussian distribution of D_y around the value D_{y0} which was obtained from

Fig. 2. (a) Correlation between the index j of a minimum and the corresponding scattering angle θ. A parabolic fit (solid line) is included. (b) Scattering on multiple slits with a sequential displacement of D_x and D_{y0}. The flight path difference Δs (dotted line) can be expressed as a function of the angle θ.

Eq. (1). The calculated intensity was folded with $B(\theta)$ being the beam profile as determined from a reference measurement. $N_{L/R}$ is a scaling factor and in addition a roughness σ is introduced. All fits to the scattering curves are included in Fig. 1c (solid lines). Except for small angles near the beam stop, the fits match well to the experimental data.

In summary, a microscopic structure in PSA debonding of a statistical copolymer, which is not resolvable by optical microscopy, was discovered by applying USAX. Asymmetric scattering pattern was interpreted in terms of multiple slit scattering, using a tilted grating. This general concept is not restricted to PSA only. It might be transferred to other systems like porous material which also shows asymmetric scattering pattern.

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