Interface and surface roughness of polymer-metal laminates
van Tijum, Redmer

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Chapter 5

Characterization of uniaxial deforming coatings

5.1 Introduction
Polymer-coated steels are commonly used in the packaging industry to protect the content of the can from the steel and vice versa. During the forming process, the coating should remain functionally in tact, i.e. it should fully adhere to the steel. An important issue during deformation of polymer-coated steels is the induced roughening of the steel substrate [1,2]. Effects of roughening on the adhesion at the interface between an amorphous polymer and steel were studied in [3,4] and chapter 6 [5]. Using qualitative polarization microscopy it was shown [4] that phenomena of deformation of the amorphous polymer layer differ considerably from the bulk behavior. As soon as the steel substrate deforms plastically, stress concentrations occur in the amorphous polymer layer near the interface that lead to localized shear bands. These shear bands already occur at strains below the yield strain of the bulk PETG. This behavior near the interface continues at higher stresses. Above the strain at yield of PETG, the deformation of the film is highly inhomogeneous with patterns of shear bands at 45 degrees with respect to the loading direction. Localized necking perpendicular to the tensile direction occurs only for very thick samples [5,7].

This chapter deals with the different aspects of the deformation of PETG laminated steel. The first part concentrates on relatively thin layers and it is aimed at examining the effect of the roughness on the inhomogeneous deformation of the coating. In the second part, the free polymer surface is studied in terms of the interface roughness of the steel, and the thickness of the polymer layer.

5.2 Strain effects in polymer coatings
Calculations performed in [5] show the evolution of the deformation in the layer, which is in qualitative agreement with experiments. Moreover, in these calculations it appears that although the energy release rate \( G \) decreases monotonically as a function of strain, the stresses acting at the interface drop if the global strain surpasses the yield strain of the amorphous polymer. It is expected that the stress field acting at the interface affects the rate at which various thermally activated degradation mechanisms (delamination, corrosion) occur [8]. Potentially a decrease in stress level near an interface (even though it occurs at a higher deformation) might be favorable in terms of the lifetime of the interface. Therefore, it is relevant to measure the stresses acting in the polymer layer as a
function of global strain. Recent theoretical advances have shown that full-field microscopic measurements of the birefringence can be executed after relatively small changes to existing optical (transmission) microscopes are made. Since the birefringence is related to the state of strain in the layer, such measurements therefore offer in principle the possibility to relate stresses in the deformed polymer layer to adhesion or delamination behavior.

This part of the chapter concentrates on in situ-birefringence measurements to quantify the differences in stress that occur in polymer layers deformed together with a steel substrate. It is important to emphasize that the technique differs from [9] in two ways: the measurements are performed in reflection, and an alternative unwrapping scheme for the optical path difference is proposed.

5.2.1 Theoretical background

Polarization microscopy is a well-known technique for studying birefringent transparent materials under stress [10]. Birefringence $\Delta n$ may be defined as $\Delta n = n_\parallel - n_\perp$, where $n_\parallel$ and $n_\perp$ are the refractive indices parallel and perpendicular to the local principal strain direction, respectively [11]. For an amorphous polymer $\Delta n$ can be expressed as a function of the orientation order parameter $\langle f \rangle$ [12]:

$$\Delta n = \Delta n_{\text{max}}\langle f \rangle. \quad (5.1)$$

When monomers are randomly distributed in space (in amorphous and unstretched state) $\langle f \rangle = 0$. Due to straining the chains will orient and $\Delta n_{\text{max}}$ will be attained when $\langle f \rangle = 1$.

Two models have been proposed for predicting $\langle f \rangle$ as a function of strain $\varepsilon$, i.e. affine and pseudo-affine models [13,14]. In the affine model flexible chains connect a network of fixed junctions. When the network is stretched it is assumed that all local deformations are proportional to the macroscopic deformations. In this case the orientation order parameter can be expressed as:

$$\langle f \rangle = \frac{1}{N} \left( \lambda^2 - \lambda^{-1} \right) \varepsilon \rightarrow 0 \approx \frac{3 \varepsilon}{5N}, \quad (5.2)$$

where $N$ is the number of random links between network points, $\lambda = \varepsilon + 1$ is the draw-ratio and $\varepsilon$ is the strain. The pseudo-affine model assumes that the structural elements are rigid. These elements are able to rotate in order to accommodate the deformation. In this case $\langle f \rangle$ can be expressed as [14]:

$$\langle f \rangle = \frac{1}{2} \left( \frac{2 \lambda^3 + 1}{\lambda^3 - 1} - \frac{3 \lambda^3}{(\lambda^3 - 1)^{3/2}} \tan^{-1} \sqrt{\lambda^3 - 1} \right) \varepsilon \rightarrow 0 \approx \frac{3 \varepsilon}{5}. \quad (5.3)$$
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In both cases at small strains $\Delta n$ is linear with the applied deformation. In fact, only the strain difference is reflected in $\Delta n$:

$$\Delta n = \Delta n_{\text{max}} \langle f(\varepsilon) \rangle = S_{\text{opt}} |\varepsilon_2 - \varepsilon_1|,$$

where $S_{\text{opt}}$ is a constant and $\varepsilon_1$ and $\varepsilon_2$ are the principal strains. It has been found that below the glass transition temperature $T_g$ pseudo-affine models show a good agreement with experiments. Moreover, assuming affine deformation $\langle f \rangle$ shows the same dependence on $\lambda$ as the stress for a amorphous polymer above $T_g$, so the well-known stress-optical rule is valid for all strains in those cases [12]:

$$\Delta n = C_{\text{opt}} |\sigma_{yy} - \sigma_{xx}|,$$

where $C_{\text{opt}}$ is the stress-optical coefficient. In general, below $T_g$ eq. (5.5) is only valid in the elastic regime.

$\Delta n$ can be measured by establishing the phase factor $\delta$:

$$\delta = \frac{2\pi L(\varepsilon) \Delta n}{\lambda},$$

where $\lambda$ is the wavelength of the radiation, $L(\varepsilon) = L_0(1 - \nu \varepsilon)$ is the thickness of the sample at a strain $\varepsilon$ and $\nu$ is the Poisson’s ratio of the coating. For full field birefringence microscopy a number of methods have recently been proposed in which a sample is illuminated with a rotating linear polarizer, and in which a circular polarizer is used as analyzer.

The relation between the $E$-field of the exiting and illuminating radiation can be described with Jones calculus, in which a matrix $M$ represents the combined effects of the optical elements on the polarization state of the radiation [e.g.15]:

$$E^T = \begin{pmatrix} E_x^T \\ E_y^T \end{pmatrix} = M^T E^T = M^T \begin{pmatrix} E_0 \cos \alpha \\ E_0 \sin \alpha \end{pmatrix},$$

where $E_x^T$ and $E_y^T$ are the $x$ and $y$ components of $E^T$, $\alpha$ is the angle between the transmission direction of the first rotating polarizer and $E_0$ is the amplitude of the illumination $E^T$ of the light-source (see Fig. 5.1). In transmission

$$M^T = M_{\text{cp}} M_{\text{r}} (-\delta) M_{\text{s}} (\phi),$$

where $M_{\text{cp}}$, $M_{\text{r}}$ and $M_{\text{s}}$ are Jones matrices representing the circular polarizer, the rotation and the sample, respectively. Furthermore, $\phi$ is the extinction angle, $\delta$ is the phase factor. The intensity $I^T (E^T)$ is by definition:

$$I^T (E^T) = E_x^T E_x^{T*} + E_y^T E_y^{T*},$$

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where * denotes the complex conjugate. The light passes a circular polarizer before detection and \( E_x^r = E_y^r = E_0^r \). Combining eqs. (5.7)–(5.9) and taking \( I_0 = \left( E_0^r \right)^2 \) results in:

\[
I^r(\alpha) = \frac{I_0}{2} (1 + |\sin \delta| \sin 2(\alpha + \phi)) .
\] (5.10)

From measurements of \( I^r(\alpha) \), the parameters \( |\sin \delta|, I_0 \) and \( \phi \) can be uniquely determined. However, to determine unambiguously \( \delta \) from \( |\sin \delta| \) an “unwrapping” technique has to be applied. The treatment of the unwrapping problem is discussed later.

The experimental setup (Fig. 5.1) used here is based on reflection microscopy. For birefringence microscopy two relevant differences exist between transmission and reflection set-ups: (1) the light path through the sample and (2) the presence of a beam splitter in the light path.

![Fig. 5.1. Ray pattern in the experimental setup.](Image)

First, the sample now consists of a birefringent coating on top of a reflective metal, rather than a birefringent layer. The Jones matrix of the sample is given by:

\[
M^R_{\text{sample}} = M_\phi M_\delta M_{-\phi} M_\text{metal} M_\delta M_{\phi} ,
\] (5.11)

Taking \( M_\text{metal} \) to represent a perfect mirror eq. (5.11) can be rewritten as:

\[
M^R_{\text{sample}} = M_\phi M_{-\phi} M_\delta M_{\phi} .
\] (5.12)

For the intensity \( I^r(\alpha) \) one finds:
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\[ I^s(\alpha) = \frac{I}{2} (1 - |\sin 2\delta| \sin 2(\alpha + \phi)) , \tag{5.13} \]

which is essentially equal to eq. (5.10), the main difference being that \(2\delta\) appears because the light travels through the specimen twice.

Secondly, the beam splitter reflects light to the sample and transmits it to the CCD camera after interaction with the sample. The effect of the beam splitter on the polarization state and on the resulting intensity can be taken into account by modeling the reflection at the beam splitter as that from an aluminum mirror with surface normal at \(45^\circ\) with the propagation direction of the light, and neglecting transmission since the propagation direction of the light is unaltered.

For the Jones matrix \(M_{bs}\) of the beam splitter one finds, after applying the Fresnel's formulae for reflection

\[
M_{bs} = \begin{pmatrix}
R_x & 0 \\
0 & R_y
\end{pmatrix} = \begin{pmatrix}
\frac{n_2^2}{2n_2^2 - 1} - 1 & 0 \\
\frac{n_2^2}{2n_2^2 - 1} + 1 & 0 \\
0 & 1 - \frac{2n_2^2}{2n_2^2 - 1} \\
0 & 1 + \frac{2n_2^2}{2n_2^2 - 1}
\end{pmatrix} \approx \begin{pmatrix}
1 & 0 \\
0 & -0.91 - 0.23i
\end{pmatrix} , \tag{5.14}
\]

where \(R_x\) and \(R_y\) are the reflection coefficients in both incident direction of the light (see Fig. 5.1), \(n_2\) is the refractive index of Al, and where the refractive index of air has been taken equal to 1. Numerical values are shown assuming \(\lambda = 589.3 \text{ nm}\) and \(n_2 = 1.44 + 5.23i\) \[16\]. At this point, all the elements of the reflection birefringence microscope have been properly defined. Combining eq. (5.8) and (5.12) results in:

\[
\vec{E}_s = \begin{pmatrix}
E_x^s \\
E_y^s
\end{pmatrix} = M_{cp} M_{bs} M_x (-\phi) M_y (2\delta) M_z (\phi) \vec{E}_m , \tag{5.15}
\]

where the incident radiation on the sample is now given by:

\[
\vec{E}_m = M_{bs} \begin{pmatrix}
E_0\cos \alpha \\
E_0\sin \alpha
\end{pmatrix} = \begin{pmatrix}
R_x E_0 \cos \alpha \\
R_y E_0 \sin \alpha
\end{pmatrix} . \tag{5.16}
\]

Due to the imaginary reflection coefficients of the beam splitter the incident light becomes slightly elliptically polarized and the intensity of the illumination of the sample is now a function of \(\alpha\):

\[
I(\vec{E}_m) = R_x R_x' E_0^2 \cos^2 \alpha + R_y R_y' E_0^2 \sin^2 \alpha = 0.875 E_0 \sin^2 \alpha + 1.013 E_0 \cos^2 \alpha . \tag{5.17}
\]

The effect of varying illumination intensity and slight ellipticity on the determination of \(\delta\) and \(\phi\) was studied in the following way. A numerical experiment
was performed in which the reflected intensity $I_r(\alpha)$ for several test-samples (each with unique values for $\delta$ and $\phi$) was calculated, as well as the intensity $I_0(\alpha)$, the reflected intensity of a reference sample (a perfect mirror of the substrate material). Subsequently the hypothesis was tested that the slight ellipticity does \textit{not} interfere with the determination of $\delta$ and $\phi$ and that the intensity $I^N(\alpha)$ resulting from a simple normalization of $I_r(\alpha)$ by $I_0(\alpha)$:

$$I^N(\alpha) = \frac{I_r(\alpha)}{I_0(\alpha)},$$

(5.18)

can serve as a base to determine $\delta$ and $\phi$. Using a series of simulated $I_r(\alpha)$ and $I_0(\alpha)$, $\delta$ and $\phi$ were determined (using the fitting procedure outlined in Appendix A [9]) and compared to input values of the simulation. It was found that this procedure leads to a maximum error in $\delta$ of about 3% and of about 5% in $\phi$. In view of other experimental uncertainties, these margins are acceptable. In practice therefore an experimental reference series $I_r(\alpha)$ was measured with a mirror-like sample of the substrate material in addition to the series $I_r(\alpha)$ of the deformed layer that were determined for a number of strain levels. At each strain, the normalized intensity $I^N(\alpha)$ was used to determine $I_0$, $\delta$ and $\phi$ as expressed in Appendix A.

5.2.2 Experimental

The samples are coated with amorphous PETG. Coatings were obtained by spin coating solutions of 2 %wt and 4 %wt PETG in chloroform on polished dog-bone shaped specimens at 250 rpm. Coating thicknesses of 4 and 8 $\mu$m were achieved by changing the two weight percentage of PETG in chloroform. After spin coating, the excess of chloroform was removed by placing the specimen in a hot-air oven at 60$^\circ$C for 2 hours. Prior to the measurements, the thickness was determined with a profilometer after locally removing the coating using a laser [17].

The measurements were performed with an \textit{in-situ} uniaxial tensile stage at a constant speed of 5 $\mu$m/s. At predefined strains, the stage was halted and an image series $I_r(\alpha, x, y)$ was measured with $\alpha = 0, 15, ..., 345^\circ$ and $(x, y)$ the pixel location. The $x$ direction is defined as the global tensile direction and is expressed as the horizontal axis in each of the following images. Prior to the measurements, a reference image series $I_r(\alpha, x, y)$ (see above) was obtained from an uncoated polished metal substrate. Images of 1376x1032 pixels were taken with a 24-bit CCD camera. All $I_r(\alpha, x, y)$ are normalized using the reference series $I_r(\alpha, x, y)$. The actual determinations of $|\sin 2\delta(x, y)|$, $\phi(x, y)$ and $I_0(x, y)$ from eq. (5.13) are explained in
Appendix A. The conversion from $|\sin 2\delta(x,y)|$ to $\Delta n(x,y)$ was performed with eq.(5.6).

The green channel of the CCD was used ($\lambda = 510$ nm) because it gave the best contrast and showed to be the least sensitive to the effects induced by beam splitter. The Poisson’s ratio $\nu$ for PETG is approximately 0.4 and the thickness $L_0$ is $4\mu$m or $8\mu$m. Typical images are shown in Fig. 5.2.

![Typical images of the intensity $I_0$ (left), phase factor $\delta$ and the extinction angle $\phi$ (right) of the 4µm thick coating at $\varepsilon = 5\%$.](image)

5.2.3 Results and discussion

As aforementioned in section 1 our interest lies with the evolution of stresses in the strained layer. The results and the discussion are organized in three parts: first the evolution of $\Delta n(\varepsilon)$, as a function of strain is discussed. This discussion entails the distribution of the measured values of $\Delta n(\varepsilon)$, the apparent stress-optical constant and strain-optical constants as well as the unwrapping technique employed. Secondly, spatial aspects of the evolution of $\Delta n(\varepsilon)$ are discussed, which leads to a discussion of the spatial correlation technique of measuring the evolution of $\Delta n(\varepsilon)$ at a fixed location in the material.

![The development of the double refraction in an area of 97x97 µm² for increasing strain: $\varepsilon = 2.5\%$ (left), 5% and 10% (right).](image)

Fig. 5.3 shows $\Delta n(x,y)$ as a function of strain. For PETG the global strain at yield is $4\% - 6\%$ [3] so at $\varepsilon = 2.5\%$ PETG is still expected to behave elastically. However, shear bands appear, indicating that locally PETG is already plastically deforming. For
increasing strains these shear bands become more pronounced. At a fixed strain $\varepsilon$ the distribution of $\Delta n(\varepsilon)$ reflects the distribution of $|\varepsilon_2 - \varepsilon_1|$ in the layer. Fig. 5.4 shows the evolution of the extremes of the distribution of $\Delta n(\varepsilon)$ as a function of $\varepsilon$. One point in the curves represents the average of either the 50 lowest ($\Delta n_{\text{min}}(\varepsilon)$) or the 50 highest ($\Delta n_{\text{max}}(\varepsilon)$) values of $\Delta n(\varepsilon)$ in the whole image. First, for low strains $\Delta n_{\text{max}}(\varepsilon)$ as well as $\Delta n_{\text{min}}(\varepsilon)$ increase linearly. This is an indication of the distribution of stresses in the coating. Second, a kink appears in both $\Delta n(\varepsilon)$ curves. For $\Delta n_{\text{max}}(\varepsilon)$ a kink appears at $\varepsilon = 7.5\%$ after which $\Delta n(\varepsilon)$ is constant. For $\Delta n_{\text{max}}(\varepsilon)$ a kink appears at $\varepsilon = 2.5\%$ leading to a lower slope.

Fig. 5.4. Left axis: Averaged double refraction $\Delta n$ as a function of the global applied strain for a selection of shear bands (○) and low $\Delta n$ areas (□). Right axis: The curve represents the stress-strain curve of PETG.

The stress-optical constant $C_{\text{opt}}$ can be determined from the following relationship:

$$\Delta n = C_{\text{opt}} |\sigma_y - \sigma_z|$$

and at yield $\Delta n_y = C_{\text{opt}} \sigma_y$, \hspace{1cm} (5.19)

where $\sigma_y$ is the yield stress. The yield stress of bulk PETG is $\sigma_y = 51 \text{ MPa}$ [3], the stress-optical constant for a representative area becomes:

$$C_{\text{opt}} = \frac{\Delta n_y}{\sigma_y} = \frac{0.013}{51 \text{ MPa}} \equiv (0.25 \pm 0.05) \text{ GPa}^{-1},$$

where the kink in the top curve in Fig. 5.4 is used for $\Delta n_y$.

In Fig. 5.4 a second regime is visible starting at $\Delta n_y \approx 0.013$. PETG has a distinct softening phase [3]. During this phase, the global decrease in stresses involves an increase in the chain alignment. Therefore, defining a second $C_{\text{opt}}$ does not make much sense. Eq. (5.20) is limited to describe the stresses up to the strain at yield, which is taken at $\varepsilon_y = 6\%$. 
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As indicated in the theory, orientation of the polymer is responsible for the changes in \( \Delta n \). It is therefore more natural to define a strain-optical coefficient:

\[
S_{opt}^{\text{elastic}} = \frac{\Delta n}{\epsilon_{yy} - \epsilon_{xx}} \approx \frac{0.013}{0.06} \approx (0.22 \pm 0.05) \quad \text{and} \quad S_{opt}^{\text{plastic}} \approx (0.10 \pm 0.02). \quad (5.21)
\]

In the literature, several studies are devoted to the birefringence of drawn PETG [17]. These studies focus on high draw ratios and therefore temperatures are above \( T_g \). At 85°C, the stress optical constant is \( C_{opt} \approx 5.5 \text{ GPa}^{-1} \). Below \( T_g \), this value drops rapidly, this indicates that our value is not an extreme case [19]. Several aspects of the analysis have to be discussed.

Unwrapping

The first point to discuss is the unwrapping method that is applied to obtain unique values of \( \Delta n \). Since \( \sin 2\delta(x, y) \) in eq. (5.13) is a periodic function, \( \delta \) has no unique solution. In literature several unwrapping techniques have been proposed [10] usually based on a comparison of \( \sin 2\delta(x, y) \) for a number of different \( \lambda \). The experiments discussed here offer an alternative method based on the deformation history of a certain site \( (x_0, y_0) \).

Fig. 5.5. The birefringence \( \Delta n \) calculated from specimen with a coating thickness of 8 \( \mu \text{m} \).
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Fig. 5.6. The unwrapping process steps expressed: □ initial measurement (sin(2δ)); ○ the wrapped signal (δ); • the derivative ∂²δ / ∂ε² and ■ the final unwrapped δ.

After converting sin 2δ(x, y) to δε(x₀, y₀), a repetitive isosceles triangle function appears for increasing ε (Fig. 5.6). We can assume that initially δε(x₀, y₀) = 0 and that on straining it starts to increase. When sin 2δ(x, y) is measured for a sufficient number of values of ε, the function will reproduce the repetitive isosceles triangle function. The minimum of the function appears at εmin when δεmin(x₀, y₀) = 0 and the maximum at εmax when δεmax(x₀, y₀) = π/4. For increasing strains, an alternating maximum and minimum appears. Another aspect of the repetitive isosceles triangle function is the change of slope of this function at each extreme. By combining both properties, the extrema can be found mathematically:

\[
\begin{align*}
\varepsilon_{\text{min}} &= \left[\delta_\varepsilon(x_0, y_0) = 0\right] \& \left[\partial^2 \delta_\varepsilon(x_0, y_0) / \partial \varepsilon^2 \gg 0\right] \quad (5.22) \\
\varepsilon_{\text{max}} &= \left[\delta_\varepsilon(x_0, y_0) = \pi/4\right] \& \left[\partial^2 \delta_\varepsilon(x_0, y_0) / \partial \varepsilon^2 \ll 0\right].
\end{align*}
\]

At each extremum, δε(x₀, y₀) should be unwrapped for all values above the specific extremum strain to create a monotonically increasing function. Because several minima and maxima could appear, we introduce an index k. First, for each element k in εmax:

\[
\delta_{\varepsilon > \varepsilon_{\text{max}}(k)}(x_0, y_0) := \pi/2 - \delta_{\varepsilon > \varepsilon_{\text{max}}(k)}(x_0, y_0), \quad (5.23)
\]

where := represents an assignment and ε > εmax(k) indicates that it should be performed element wise for all strains larger than εmax(k). Second, for each element k in εmin:

\[
\delta_{\varepsilon < \varepsilon_{\text{min}}(k)}(x_0, y_0) := k\pi - \delta_{\varepsilon < \varepsilon_{\text{min}}(k)}(x_0, y_0) \quad (5.24)
\]

After both steps the function δε(x₀, y₀) is a monotonically increasing as a function of strain.
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In order to measure the evolution of $\delta_i(x_0, y_0)$, the position $(x_0(\epsilon), y_0(\epsilon))$ has to be known as a function of strain. This is achieved using image correlation techniques on $I_0(x(\epsilon), y(\epsilon))$. The image correlation technique is able to determine displacements between two (sub)-images. In our experiments the deformations are inhomogeneous. This is taken into account by correlating a raster of sub-images of a size of 32x32 pixels (Fig. 5.7). For the point at the center of each sub-image a displacement vector is found. Combining the displacement vectors of the whole set of sub-images enables us to use interpolation techniques to find $(x_0(\epsilon), y_0(\epsilon))$.

Fig. 5.7 shows a raster of correlated centre-points for two different stages of the straining process. Fig. 5.8 shows the necessity of unwrapping. If the average of a selection of 50 points from the 8 $\mu$m coated specimen is taken, problems appear for increasing strains. The curve in Fig. 5.8 starts to decrease at $\epsilon = 5\%$. After unwrapping each individual point, a correct graph is created. The process of unwrapping becomes an issue for thicker coatings or higher strains.

Fig. 5.7. Two correlated intensity images for two different stages ($\epsilon = 0\%$ and $5\%$) of the 4 $\mu$m thick coating. The dots denote the correlated locations initially with a distance of 25 pixels (roughly 8 $\mu$m). Clearly visible is the deformation of the surface between both stages.

Fig. 5.8. Phase factor $\delta$ for an 8 $\mu$m thick sample averaged over 50 points of a shear band expressed (○) with and (□) without unwrapping.
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Spatial variations of $\Delta n$

To give an insight into $\Delta n(\varepsilon)$ a line profile is made between two shear bands (Fig. 5.9). The left- and right-hand side of the line profile correspond to locations of a shear band, whereas the centre of a line profile can be defined as a relaxation area (see lower curve in Fig. 5.4). For increasing strains, the spacing between two subsequent lines in Fig. 5.9 changes. A large spacing represents an increasing $\Delta n(\varepsilon)$, whereas two subsequent curves on top of each other can be defined as constant birefringence. The elastic regime is visible for the shear band up to $\varepsilon = 2.5\%$. Fig. 5.9 shows large changes in $\Delta n(\varepsilon)$ for each individual $\varepsilon$. This reveals the localizations that occur in polymer coatings. Close to the shear-bands, $\Delta n$ doubles on a scale of a few microns. This emphasizes the importance of localization. The cause of the contrast variations of $\Delta n$ can have two sources. The extrinsic source is related to roughness. The standard deviation of the surface defined by the rms roughness $w$ is linearly related to $\varepsilon$ and the grain size $d$ [1]:

$$w \approx 0.2d\varepsilon.$$  \hspace{1cm} (5.25)

The relationship in eq. (5.25) can only be employed for metals without texture. Although in our case the stainless steel is textured [5], eq. (5.25) gives a good approximation of the introduced roughness at the strain levels we use. In our experiments the number average grain size is determined by EBSD and found to be $d = 11.7 \mu m$. Therefore, the coating thickness is at least one order larger than $w$. Nevertheless, the roughness is the primary source for the introduction of shear bands [5]. At the interface, shear bands originate, which combine at a certain distance from the interface to wider and less intense bands (see section 5.3.3 and [7]). Since roughness is a surface effect and the birefringence is a measured over the thickness of the coating, relatively thin coatings will exhibit mainly the effects of roughness, whereas thicker coatings show more bulk properties.

The intrinsic variations of $\Delta n$ are presented in Fig. 5.4. The lower curve represents the relaxed areas. At $\varepsilon = 7.5\%$, a kink in the slope appears and the birefringence becomes constant, $\Delta n_i$. The constant birefringence implies no further orientation in these regions. The global applied strain is localized in shear bands. Secondly, the relaxed areas are still elastic, because $\Delta n_i < \Delta n_i$. Both aspects are examples of necking found for the deformation process of polymer tensile bars [20]. This suggests that the intrinsic variations are related to the existence of a softening region.
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For thicker coatings, the effect of localization will be similar near the interface [5,7], however for increasing thicknesses, the variations of $\Delta n$ appear to decrease. As indicated PETG is unstable at yielding and a small disturbance will generate a shear band. For thicker coatings, this process is not different. As expressed in [5,7], the interaction between individual shear bands will create larger less pronounced shear bands through the coating thickness. In the experiments, the average $\Delta n$ across the thickness is measured. Therefore, the variations in $\Delta n$ close to the interface (Fig. 5.10a) are not so obvious. Taking the average over the thickness will therefore result in the image displayed in Fig. 5.10b.

Coating thickness

For thicker coatings, the effect of localization will be similar near the interface [5,7], however for increasing thicknesses, the variations of $\Delta n$ appear to decrease. As indicated PETG is unstable at yielding and a small disturbance will generate a shear band. For thicker coatings, this process is not different. As expressed in [5,7], the interaction between individual shear bands will create larger less pronounced shear bands through the coating thickness. In the experiments, the average $\Delta n$ across the thickness is measured. Therefore, the variations in $\Delta n$ close to the interface (Fig. 5.10a) are not so obvious. Taking the average over the thickness will therefore result in the image displayed in Fig. 5.10b.

Fig. 5.9. Line profiles of $\Delta n$ as a function of $\varepsilon$. The highest value of $\Delta n$ corresponds with a shear band and is typically shown in Fig. 5.4.

Fig. 5.10. Double refraction at $\varepsilon = 2.5\%$ for a coating of: a. 4 $\mu$m and b. 8 $\mu$m.
In the next section the deformation inside the coating is studied in an alternative way, relating the roughness of the surface to the roughness at the interface. Confocal white light microscopy is used to investigate the surface geometry.

### 5.3 On the evolution of free polymer surface roughness

The evolution of surface roughness of metals during deformation and its relation to microstructure and sample geometry have been the subject of a number of recent papers, both experimental and numerical by us [1,2,21] and other researchers [22]. Experimentally it was found that the roughness on the surface of a uniaxially deforming metal can effectively be described by three parameters: the rms roughness amplitude $w$ beyond a certain lateral correlation length $\xi$, and a Hurst exponent $H$ characterizing a self-affine geometry below $\xi$ [2]. The set of three parameters can be determined from experimental measurements of the sample surface $h(r, \varepsilon)$ at a strain $\varepsilon$ and at the position $r$. A height-height correlation function $C(r, \varepsilon)$ of a surface may be defined as [23]:

$$C(r, \varepsilon) = \langle h(r, \varepsilon) h(0, \varepsilon) \rangle,$$  \hspace{1cm} (5.26)

It has been shown experimentally [1,5,24,25] that for all strains $C(r, \varepsilon)$ of a surface of a uniaxially deforming metal can be approximated by

$$C(r, \varepsilon) = w(\varepsilon)^2 \exp[-(r/\xi(\varepsilon))^{2H(\varepsilon)}].$$  \hspace{1cm} (5.27)

The correlation below $\xi$ is due to in-plane spatial correlations in the slip patterns inside the grains and due to texture. In the absence of texture, $\xi$ is approximately equal to the grain size. Parameterized fits for $w(\varepsilon)$, $H(\varepsilon)$ and $\xi(\varepsilon)$ as a function of the applied strain (see also [1,25]) can be made.

The evolution of roughness at the surface of a polymeric coating on a deforming metal has not been treated in these terms and the extension to that case is the subject of this part of the chapter. Numerical and experimental results are presented that illustrate the evolution of the roughness at the free surface of amorphous polymer supported by a metal substrate. The surface roughness is introduced by uniaxial deformation of the metal substrate. A similar system is used here of PETG coated on stainless steel.

#### 5.3.1 Experimental

Polished stainless steel disks with a diameter of 60 mm and a thickness of 500 µm were spin coated with PETG. 10 %wt PETG and 0.5 %wt TiO$_2$ dissolved in chloroform. TiO$_2$ was used as whitener of the coating to prevent reflection of the metal substrate and
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<table>
<thead>
<tr>
<th>ε = 5%</th>
<th>Metal substrate</th>
<th>Initial thickness</th>
<th>Initial thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>27 µm</td>
<td>58 µm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5.11. Measurements of the deformation of polymer coated laminate. The metal surface is created by removing locally the coating with a nanosecond laser. The statistical characteristics of the metal were not altered by the laser.

allow optical height measurements. Spin coating at 250 rpm resulted in a coating thickness of roughly 15 µm. Thicker coatings were achieved by repeating the spin coating process. Dog-bone shaped tensile bars were created by laser-cutting. The resulting specimens were placed in a hot-air oven at 60 °C for 2 hours in order to remove solvents. The uniaxial deformation was achieved with an in-situ tensile stage at a constant rate of 5 µm/s (corresponding with an initial strain rate \( \dot{\varepsilon} = 2 \cdot 10^{-4} \)). A white light confocal microscope was used to measure the surface morphology at predefined strains at different locations (at least 4). The thickness of the layers was measured with
the same microscope after locally removing the coating with an Expla Nd:YAG IR laser [17].

Fig. 5.11 shows images of the substrate morphology and of two coated samples at increasing strains. In a qualitative sense, a number of aspects are noteworthy. First, the amplitude of the surface roughness increases with increasing strain (see also Fig. 5.12). Second, surface profiles before and after a step in strain are highly correlated [1]. Third, the surface profiles of the coated samples appear “smoother” than that of the substrate. Note, that the black distinct areas in Fig. 5.11 are undetected surfaces by the confocal microscope. These areas are removed from further analysis.

To obtain a quantitative picture, we study the evolution of the height-height correlation function as expressed in eqs. (5.26) and (5.27) on these samples as a function strain. Specifically we determined the characteristics of \( w(\varepsilon) \), \( H(\varepsilon) \) and \( \xi(\varepsilon) \) for coated and uncoated samples. Fig. 5.12 shows \( w(\varepsilon) \) of all five samples. After polishing and spin coating, the surfaces have a small initial rms roughness \( w_m(0) \), which is subtracted from the measured roughness \( w_m(\varepsilon) \) according to:

\[
w(\varepsilon) = \sqrt{w_m^2(\varepsilon) - w_m^2(0)}.
\]  

\( w_m(0) \) is also shown in Fig. 5.12 and it is seen to be small. The data are fitted in a least square sense to the following function

\[
w(\varepsilon) = w_{\text{sat}}(1 - e^{-C\varepsilon}),
\]  

Fig. 5.12. Rms roughness as a function of the global strain for different coating thicknesses: ★ metal substrate, ▽ 13 \( \mu \)m, ■ 27 \( \mu \)m, ● 50 \( \mu \)m and △ 58 \( \mu \)m. The arrow points to the initial rms roughness \( w_m(0) \) of each specimen.
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where the stainless steel is defined by $w_{sat} = 1.1 \, \mu m$ and $C_i = 6.1$. This functional form is used by the numerical simulation to describe the roughness (see section 5.3.2).

The uppermost curve in Fig. 5.12 represents $w(\varepsilon)$ for the metal substrate. Compared to that curve a decrease in $w(\varepsilon)$ is observed for increasing coating thickness up to $d_o = 27 \, \mu m$. It is interesting to see that for $d_o = 50 \, \mu m$ and $d_o = 58 \, \mu m$ $w(\varepsilon)$ is slightly higher than for $d_o = 27 \, \mu m$. Each dot in Fig. 5.12 is the average of measurements of at least four different areas on the surface and therefore shows the standard deviation over $10^6$ individual surface points. Furthermore, care is taken to measure the same surface areas for each strain.

For the Hurst exponent $H(\varepsilon)$ the following is found (Fig. 5.13a). At small strains, $H(\varepsilon)$ is determined by the initial surface roughness, as a result of the polishing or spin coating procedure. The typical surface characteristics of the plastic deformation become visible after a few percent of strain (Fig. 5.11). In general $H(\varepsilon)$ tends to a constant value for higher strains:

$$H(\varepsilon) \rightarrow H_0.$$  \hspace{1cm} (5.30)

For the metal substrate $H_0 = 0.6$. For the coated samples $H_0$ increases as a function of coating thickness.

For the coated samples $H_0$ increases as a function of coating thickness.

![Fig. 5.13a. Hurst exponent as a function of the initial coating thickness.](image)

![Fig. 5.13b. Correlation length $\xi$ as a function of the initial coating thickness, where $\xi_0$ is the initial surface roughness of the metal substrate.](image)

A small value of $H_0$ results in larger fluctuations at small length scales. The profiles in Fig. 5.11 show fewer fluctuations on a short length scale for increasing coating thickness, which is therefore in agreement with the trend in Fig. 5.13a. Fig. 5.13a also expresses a decrease of $H_0$ for the thickest coating $d_o = 58 \, \mu m$. For this coating, it implies that the fluctuations on a short length scale increases. The origin of these fluctuations is shown in Fig. 5.11. First, this coating has a relatively large amount
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of TiO\textsubscript{2} particles at the free surface. Second, a thick coating shows commonly small local necks perpendicular to the tensile direction. Both arguments lead to more fluctuations and therefore to a decrease of $H_\alpha$. Nevertheless, the effect is primarily visible in the Hurst exponent whereas the other parameters ($w$ and $\xi$) are more of macroscopic nature.

For the metal substrate the $\xi(\varepsilon)$ increases with strain in the tensile direction:

$$\xi(\varepsilon) = \xi_0 (1 + \varepsilon),$$  \hspace{2cm} (5.31)

where $\xi_0 = 35 \, \mu m$. Fig. 5.13b expresses $\xi_0$ as a function of the thickness of the polymer layer. The thinner samples show a more or less constant value, whereas the two thickest coating show a clear increase. The physical reasons for the trends measured above are not clear a priori and in an attempt to clarify them a two-dimensional numerical simulation of a polymer layer co-deforming with a metal substrate is performed. The resulting geometry of the deformed polymer surface has been analyzed with the same tools as the experimental data.

5.3.2 Numerical simulations

The numerical model describes the interaction between steel and PETG and will capture the following three aspects: Polymer deformation [26]; roughening of the metal surface [27]; interaction between metal and polymer across the surface [30,31]. The representation of the PETG layer is a finite element model (FEM) built from quadrilaterals representing an initial size of 1x1 $\mu m^2$ [21]. The initial length of the system is 2049 $\mu m$ and the initial thickness of the PETG film is $d_0$. In the calculations, the ‘metal’ substrate is assumed to be fully rigid. This is a reasonable approximation, since the elastic modulus of steel is typical of the order of 200 GPa and that of amorphous polymers is of the order of 1 GPa. A detailed description of the model can be found in [21]. Fig. 5.14 shows different stages of the constitutive behavior of the polymer. The polymer is elastic up to yield (top), after the polymer starts to soften (middle). In this regime, shear bands occur as a result of localization. Eventually the hardening phase will stop the localization (bottom).

One of the simplifications in our approach is to parameterize the roughness evolution of a metal surface as a function of strain, and to assume that the roughness evolution at a polymer-metal interface is essentially identical to this because of the large difference in elastic moduli of typical metals (\~100s of GPa) and amorphous polymers (\~1 GPa). A recursive refinement algorithm [27] was used to simulate surfaces with the characteristics described by eq. (5.29)-(5.31). A detailed example of the roughness evolution in the numerical model is displayed in [21].
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Fig. 5.14. Finite element calculations showing $\sigma_{nn}$ in MPa in the polymer layer for strains in the elastic, softening and hardening region of the polymer stress-strain curve.

In finite element models stress-separation laws are commonly known as “cohesive zones” and different kinds have been discussed in the literature [28,29]. In the numerical calculations presented here, the interface was implemented as a rate-independent mixed-mode cohesive zone of the type described in [30,31]. This type defines coupled stress separation laws $\sigma_n(\Delta_n, \Delta_t)$ (tractions) and $\tau(\Delta_n, \Delta_t)$ (shear stresses) at the interface, with $\Delta_n$ and $\Delta_t$ coordinates normal and parallel to the interface respectively. The distance $\Delta_0$ is defined as the point at which the opening stress $\sigma_n$ attains its maximum value $\sigma_{n}^{\text{max}}$. Unless stated otherwise the parameters used for the cohesive zone in this chapter are: normal-to-shear stress ratio $\sigma_{n}^{\text{max}} / \tau_{t}^{\text{max}} = 0.75$, interface energy $G_{cz} = 30$ J/m$^2$, working distance $\Delta_0 = 300$ nm and $\sigma_{n}^{\text{max}} = 36.8$ MPa.

In the calculations, the laminate is loaded uniaxially up to strains of 50% (in steps of 0.1%) assuming plane strain. At each step the following boundary conditions (see Fig. 5.14) are imposed on the PETG and the cohesive zone. At the side of the PETG at $x = 0$, the coating is fixed along $x$ while displacements along $y$ are free. At $x = L(\epsilon)$, the displacements in $x$ direction are fixed at $x = L(\epsilon)$ and along $y$ are free. Along the interface, displacements in the substrate are constrained in all directions. Displacements in the polymer are not restricted and coupled to those in the substrate by the stress-separation laws incorporated in the cohesive zone. At each strain step the positions of the substrate nodes are updated in $x$ (to reflect the increase in strain) and $y$ (to reflect the increase in roughness).
5.3.3 Results and discussion

Fig. 5.15a shows the results of a simulation for a model laminate in which the roughness at the interface consists simply of an array of regularly spaced $\lambda$ steps of height $\Delta y$. The interface has two characteristic lengths, i.e. one along the interface that can be thought of as an analogue to $\xi = \lambda$ and one perpendicular to the interface that can be thought of as $w = \Delta y/2$. Note that for this interface geometry the height-height correlation function is not a smooth function and due to the fact that the periodicity is not well defined beyond $\xi$. Fig. 5.15a shows the final geometry of planes initially parallel to the interface at regular (approximately 1 $\mu$m) intervals. The bottom line in the figure represents the metal surface and the second line represents points that are initially 1 $\mu$m above the interface, and so on.

A number of interesting phenomena appear. The steps at the surface cause displacements in the polymer layer. In essence, a step initiates shear bands in the polymer that extend at an angle of 45° towards the free surface (indicated with arrows in Fig. 5.15a). The shear bands may be thought to “transport” the step to the surface. Two types of steps may be defined: steps “up” or “+” and steps “down” or “-”. The shear-bands may be characterized in a similar way (see Fig. 5.15a). At the interface steps of opposite sign alternate. Both types of steps generate two shear bands of equal type that extend from the interface in directions perpendicular to each other. This can be clearly seen from the deformation of the planes initially parallel to the interface, especially those closest to the interface. These are indicated in the figure by the arrows. One of the shear bands is somewhat more pronounced than the other. Two effects determine the roughness of a plane at a certain distance from the interface. First, some of the shear
bands “transporting” the steps will intersect at a certain distance away from the interface. This means that there is interference between steps that are first separated at some distance (with periodicity $\ell$) at the interface. It is interesting to note that both shear bands with unlike sign as well as shear bands with like sign may cross. At the points of intersection, a step will result with a height and sign that is determined simply by the summation of the two steps being transmitted by the shear bands. At the points of intersection of shear bands with like signs the resulting step will be larger and at the points of intersection of steps with unlike sign the resulting step will be smaller. In this particular case at all steps have equal heights and therefore at a distance of the interface $h = n\ell/2 \ (n = \text{odd})$ the resulting amplitude is 0. (At these distances heights all intersections are between shear bands of unlike sign. On the other hand at a distance of $h = n\ell/2 \ (n = \text{even})$ the interaction is between steps of like sign and the resulting step height increases and actually becomes larger than the height at the interface.

Second, the step shape changes. High spatial frequencies are gradually disappearing as the distance to the interface increases. Implying that the step becomes ever more delocalized with increasing distance to the roughening interface. Eventually, if the width of the delocalized steps is much larger than $\ell$ steps of unlike sign will always overlap and the roughness will tend to go to zero.

From these observations it would appear that $w(d)$ at the free surface of a polymer coating on a plastically deforming metal surface may be a non-monotonic function of coating thickness $d$ (see Fig. 5.15b).

Also, the observations suggest a relation between the correlation length $\xi$ at a self-affine deforming surface and $w(d)$. Recalling the interpretation of the interface discussed here as a model interface with $\xi = \ell$ and $w = \Delta y/2$, it suggests that the ratio $d(\varepsilon)/\xi(\varepsilon)$ between the layer thickness $d(\varepsilon)$ and the correlation length $\xi(\varepsilon)$ at the interface of a deforming polymer-metal laminate is important in the roughening of the outer surfaces. Damped oscillations of $w(d)$ may be expected to occur with a period of $d(\varepsilon)/\xi(\varepsilon)$. Clearly, on a self-affine interface details (steps) are present at many length scales and the situation may be expected to less clear-cut.

Fig. 5.14 shows calculations for a more realistic two-dimensional self-affine interface with $H_o = 0.6$ and $\xi_o = 35$ for $d_o = 60 \mu m$. Fig. 5.14 shows $\sigma_{\varepsilon_o}$ at applied strains at which the bulk polymer should be in the elastic, softening and hardening regime respectively [3,20]. In the elastic regime stresses are rather homogeneous throughout the polymer. The effect of the roughness is expressed by the deviations from the applied stress, which are more prominent closer to the interface. In the softening regime strains and stresses are inhomogeneous and concentrated in shear bands. In this regime the effect of the roughening interface on the stress distribution in the polymer and the
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The different regimes affect the previously described framework of parameters \( w \), \( \xi \) and \( H \). The first parameter \( w \) is expressed in Fig. 5.16 as a function of strain for a number of thicknesses and Fig. 5.17a as a function of the thickness \( d = d_0(1+\nu \varepsilon) \) in three regimes of the deformation: elastic \((\varepsilon < \varepsilon_y)\), softening \((\varepsilon_y < \varepsilon < \varepsilon_H)\) and hardening \((\varepsilon > \varepsilon_H)\).

Fig. 5.16 and Fig. 5.17a show that in the elastic regime \((\varepsilon < \varepsilon_y)\), the slope of \( w_{PETG}(\varepsilon) \) is approximately constant as a function of strain, and that it decreases monotonically as a function of coating thickness. So, for \( \varepsilon < \varepsilon_y \) is the rms roughness \( w \) “absorbed” by the coating (Fig. 5.17a). In the softening regime \( \varepsilon_y < \varepsilon < \varepsilon_H \) the situation is more complex. In this regime, the coating develops the shear-bands that transmit the height differences generated at the interface, and (as discussed above) spatially interaction between separated interface artifacts is possible. For thin (i.e. \( d_0 \ll \xi \)) coatings the effect of shear bands is limited and therefore these have a constant \( w_{PETG}(\varepsilon)/w(\varepsilon) \) ratio for all \( \varepsilon \).

Thicker coatings (i.e. \( d_0 \gg \xi \)) show a decrease in \( w_{PETG}(\varepsilon)/w(\varepsilon) \) immediately after \( \varepsilon \) reaches \( \varepsilon_y \), followed by a slight fluctuation of the roughness for increasing strains. For these coatings, an increase in \( w_{PETG}(\varepsilon)/w(\varepsilon) \) can be observed up to values above 1. This effect was also observed for the model interface discussed earlier (see Fig. 5.15b). Focusing on the results of \( \varepsilon = 20\% \) in Fig. 5.15b and Fig. 5.17a, a few interesting aspects appear. In both figures the minimum appears at \( d(\varepsilon) = \xi(\varepsilon)/2 \) and
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![Graph showing simulated PETG (ε)/w(ε) as a function of thickness for different strains.

Fig. 5.17a. Simulated \( w_{\text{PETG}}(\varepsilon)/w(\varepsilon) \) as a function of thickness for different strains: \( \nabla \varepsilon = 2\% \), ■ \( \varepsilon = 20\% \) and • \( \varepsilon = 50\% \).

reaches a value above 1 at \( d(\varepsilon) = \xi(\varepsilon) \). This emphasizes the relationship between \( \xi \) and the coating thickness \( d_o \).

Fig. 5.17a shows a second kink in \( w_{\text{PETG}}(\varepsilon)/w(\varepsilon) \) at \( d(\varepsilon) = \xi(\varepsilon) \), which is different from the model system in Fig. 5.15b. The simulated surface can be seen as an assembly of many steps, with different height. All these steps will interact. Below \( \xi(\varepsilon) \), the system is well defined and correlated (similar to the simplified step function). Beyond \( \xi(\varepsilon) \), the surface is described by first order statistics (randomness) without any correlation. In general, the addition of two random steps will lead to a higher \( w(\varepsilon) \) than in the case of two correlated steps because the statistical height difference for correlated steps is by definition smaller (see eq. (5.27)). In the case of \( d(\varepsilon) < \xi(\varepsilon) \), only correlated steps will interact and therefore Fig. 5.15b and Fig. 5.17a should show the same trend. This effect is expressed by the second kink at \( d(\varepsilon) = \xi(\varepsilon) \).

For the hardening regime (\( \varepsilon > \varepsilon_H \)), \( w_{\text{PETG}}(\varepsilon)/w(\varepsilon) \) decreases as a function of \( d(\varepsilon) \). This situation is similar to that in the elastic case. All curves approximate to the value of \( w_{\text{PETG}}(\varepsilon)/w(\varepsilon) \) that existed in the elastic regime (see Fig. 5.16). At \( \varepsilon = 50\% \), the coating with \( d_o = 60 \mu m \) has not reached the elastic value. As a consequence a dip appears in the \( \varepsilon = 50\% \) curve in Fig. 5.17a. For increasing strain this line will homogenously decrease like the elastic curve (\( \varepsilon = 2\% \)).

Apart from the rms roughness, the evolution of the Hurst exponent and the correlation length can also be studied. Results are shown in Fig. 5.18a and Fig. 5.18b, respectively. The evolution of the Hurst exponent as a function of thickness is shown in Fig. 5.18a. It can be seen that \( H_o \) saturates to a value of 1. The initial steep jump at \( d_o = 0 \mu m \) is due to the cohesive zone, which is soft compared to the PETG coating. It is important is to note how fast \( H_o \) increases in the first micrometers. It shows how well

![Graph showing experimental PETG (ε)/w(ε) for different stages of the deformation process.

Fig. 5.17b. Experimental \( w_{\text{PETG}}(\varepsilon)/w(\varepsilon) \) for different stages of the deformation process: \( \Delta \varepsilon = 16\% \) and ■ \( \varepsilon = 38\% \).]
the polymer coating is able to absorb the high frequency oscillations applied at the interface. Fig. 5.18b shows an increasing correlation length for increasing thicknesses. A similar jump as in Fig. 5.18a is observed at $d_0 = 0 \mu m$. The curve increases monotonically as a function of thickness. If the interface is described in terms of steps, the free polymer surface will combine these steps. For increasing coating thickness, the number of contributing step increases. Therefore, the coating thickness leads to an increase in the correlation length.

Fig. 5.18a. Hurst exponent $H$ as a function of the initial coating thickness found in the numerical simulation.

Fig. 5.18b. Correlation length $\xi$ as a function of the initial coating thickness.

5.3.4 Experiment vs. simulation

With the insight gained from the numerical simulations the experimental results are interpreted as follows. In the simulations a non-monotonic increase is found for $w(\varepsilon)$ as a function of strain (Fig. 5.16). The three regimes of polymer deformation are clearly visible in the evolution of $w(\varepsilon)$ for rather thick layers, but not for thin layers that deform in a more homogeneous way. This striking result is in disagreement with the experimental findings in Fig. 5.12. In the experiment $w(\varepsilon)$ increases monotonically for all thicknesses studied and the distinction between the expected elastic, softening and hardening regimes of polymer deformation was not observed. We note that the intersection of shear-bands that leads to the fluctuations in $w(\varepsilon)$ as a function of thickness in the model may not be as important in the experiment as it is in the simulation. The simulation is a two-dimensional plain strain representation of a three-dimensional system. In the simulation only 2 planes with a high resolved shear stress exists at $45^\circ$ to the tensile direction. In the simulation these shear-bands represent the only mechanism for the coating to adapt its shape to the roughening substrate and to
adapt its shape to the uniaxial deformation imposed. Clearly, in the experiment more sets of planes with high resolved shear stresses are available. Actually 4 shear band planes may exist and as is obvious from the microscopic measurements (see Fig. 5.11) all of them are important in the deformation of the layer. In fact, a certain part of the deformation of the layer in the softening regime is carried by sets of shear bands not present in the simulation. This implies effectively that the roughening in the experiment is expected to be less dramatic than in the simulation, and explains the qualitative difference between calculation and experiment.

Nevertheless, the mechanism found in the simulations is also active in the experiment. Fig. 5.17b does show a non-monotonic behavior as a function of thickness, which in fact is in agreement with the simulation (Fig. 5.17a). In both experimental and simulation, the thickness influences $w(e)$. The Hurst exponent $H_o$ in both systems shows the same trend towards unity (Fig. 5.13a and Fig. 5.18a).

Some differences can be explained from the fact that experimentally the surfaces were initially not flat (see Fig. 5.11). First, small amount of TiO$_2$ particles appear at the coating surfaces. Second, the thickest coating shows many small cracks perpendicular to the tensile direction. Both arguments result in a large fluctuation in the surface height on a short lateral length scale, implying a decrease of $H_o$. $\xi_0$ behaves differently in the experiment compared to the simulations (Fig. 5.13b and Fig. 5.18b). The experiment shows a constant correlation length for thickness up to $\xi$. For larger thicknesses the correlation length increases as a function of thickness. The calculations show a correlation length that increases continuously. The 2D character of the model is the cause for this difference. Both experiment and simulation have a maximum thickness of $d_o = 60\,\mu m$ and at higher strains follows $\xi(e) = d(e)$. The results of experiments and simulations show that interesting aspects should happen above this thickness.

5.4 Conclusion

In this chapter the properties of PETG coated stainless steel is analyzed with two different experimental techniques. The first technique used focuses on the local deformation of relative thin polymer coatings. Birefringence reflection microscopy is able to characterize strain fields of transparent supported coatings. From the characterization of PETG coated stainless steel the following conclusions can be drawn: Strain localization appears far below the strain at macroscopic yielding. The surface roughness of the substrate is the driving force for the localization. The localization results for thin coatings in elastic regions at global strains of at least 18%. For thicker coatings the increasing thickness results in a decrease of the contrast in the birefringence. Nevertheless, it is concluded that the appearing shear bands are much
wider and a variety of the small sharp shear bands at the interface are still present. Therefore, the coating thickness does not alter the mechanisms acting at the interface.

Simulations and experiments are employed to characterize the outer surface roughness of a polymer laminated stainless steel were employed. From the combination of both techniques the following trends in surface roughness can be formulated. The strain dependence of the rms roughness amplitude \( w(\varepsilon) \) is complex and depends mostly on the stress-strain characteristics of the polymer film in combination with the available planes with a high resolved shear stress. Both the simulation and the experiment show a relatively low value for \( \xi(\varepsilon) \approx d(\varepsilon) \). In the elastic and hardening regime \( w(\varepsilon) \) decreases as a function of the thickness. The Hurst exponent \( H_0 \) increases towards unity for increasing thickness. The correlation length \( \xi_0 \) can be defined as the largest length scale in the system: coating thickness or lateral correlation length of the interface. In general, an increase in the coating thickness results in a smoother free polymer surface. This is expressed by the combination of \( H_0 = 1 \) and \( \xi_0 = d_0 \).

The combination of both techniques, supported by calculations, showed to be a powerful combination to analyze this complex PETG laminated steel. Both techniques show the effects of the metal surface roughness on the PETG coating. Independent of the coating thickness the shear bands originate at the interface.

### 5.5 Appendix A

In order to extract the \( I_0(x, y) \), \( \delta(x, y) \) and \( \phi(x, y) \) from the normalized intensities \( I^N(\alpha, x, y) \) we rewrite [9] eq. (5.13):

\[
I^N(\alpha) = \frac{1}{4} I_0 - \frac{1}{4} I_0 \sin 2\delta \cos 2\phi \sin 2\alpha - \frac{1}{4} I_0 \sin 2\delta \sin 2\phi \cos 2\alpha. \tag{5.32}
\]

This equation can be fitted in a linear least-square procedure to the following function [9]:

\[
I^N(\alpha) = a_0 + a_1 \sin 2\alpha + a_2 \cos 2\alpha, \tag{5.33}
\]

where:

\[
a_0 = \frac{1}{4} I_0, \quad a_1 = -\frac{1}{4} I_0 \sin 2\delta \cos 2\phi \quad \text{and} \quad a_2 = -\frac{1}{4} I_0 \sin 2\delta \sin 2\phi \tag{5.34}
\]

The constants in eq. (5.33) can be calculated by rotating the linear polarizer with fixed steps to a multiple of \( \pi \) with a total of \( N \) values for \( \alpha \):

\[
a_0 = \frac{1}{N} \sum_{n=0}^{N-1} I^N(\alpha_n), \quad a_1 = \frac{1}{N} \sum_{n=0}^{N-1} I^N(\alpha_n) \sin(2\alpha_n) \quad \text{and} \quad a_2 = \frac{1}{N} \sum_{n=0}^{N-1} I^N(\alpha_n) \cos(2\alpha_n). \tag{5.35}
\]

The variables of interest are calculated from eq.(5.35):

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\[ I_n = 2a_n, \quad |\sin 2\delta| = \frac{\sqrt{a_1^2 + a_2^2}}{a_0} \quad \text{and} \quad \phi = \arctan \left( \frac{a_2}{a_1} \right) \quad (5.36) \]

This procedure is applied to every pixel \((x, y)\) and subsequently images \(|\sin 2\delta(x, y)|\), \(\phi(x, y)\) and \(I_0(x, y)\) are made.

5.6 References

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