Interface and surface roughness of polymer-metal laminates

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 2
Basic concepts

2.1 Introduction
This chapter deals with the basic concepts that are used in this thesis. The materials object in our work is a polymer-coated steel laminate. In the first part the various techniques are delineated. The second part is devoted to the material system. Polymer coated steel can be divided in three components: the polymer coating, the metal substrate and the interface. In particular, emphasis is put on the deformation process. Finally, a numerical model that has been used to support the experiments, will be explained.

2.2 Experimental techniques

2.2.1 White light confocal microscopy
In recent years the technique of confocal microscopy, first described by Minsky [1], has become a powerful tool for surface characterization. The basic principle of confocal microscopy is depicted in Fig. 2.1. Light emitted from a point light source is imaged into the focal plane of the microscope objective. An in focus specimen location leads to a maximum light flux through the detector pinhole, whereas light from defocused planes is partly suppressed.

The depth response \( I(z) \) of the detector can be written as a function of the relative position of the focal plane \( z \) [3]:

\[
I(z) = I_0 \left( \sin \left[ \frac{2\pi z}{\lambda} \left(1 - \cos(\alpha)\right) \right] \right)^2,
\]

where \( \lambda \) is the wavelength of the light, \( I_0 \) is the measured intensity by the detector at \( z = 0 \) and \( \alpha \) is the aperture angle of the objective lens. The maximum aperture angle \( \alpha_{\text{max}} \) of the objective can be calculated from the numerical aperture \( NA \) :

\[
\alpha_{\text{max}} = \frac{1}{2} \sin^{-1}(NA)
\]

(2.2)
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![Diagram of confocal microscope principle](image)

**Fig. 2.1. Basic principle of the confocal microscope [2].**

The maximum slope that can be measured is equal to the maximum aperture angle \( \alpha_{\text{max}} \). Significant for the depth response is the full width at half maximum [2], which is

\[
\text{FWHM} = \frac{0.443 \lambda}{1 - \cos \alpha}.
\]  

(2.3)

During a scan along the \( z \) direction, the intensity is measured in discrete steps \( I(z_k) \). The relative height \( h \) of the surface can be calculated from the depth response curve \( I(z_k) \) using the centre of gravity of the peak in eq. (2.1):

\[
h = \frac{\sum_{z_k \in \text{FWHM}} I(z_k) z_k}{\sum_{z_k \in \text{FWHM}} I(z_k)}.
\]  

(2.4)

Various designs of confocal microscopes for the evaluation of 3D data are possible. The technique described so far is time consuming because for every surface point an independent scan along the \( z \) direction should be performed. By means of a Nipkow disk with a multi pinhole mask one is able to circumvent this drawback. In the experimental setup, a NanoFocus µSurf confocal microscope from NanoFocus Meßtechnik GmbH is used. This confocal microscope has a fast rotating Nipkow disk mounted between the objective lens and the beam splitter. The Nipkow disk replaces the confocal aperture detector pinhole (Fig. 2.1). The confocal microscope used is equipped with a Nipkow disk with pinholes of 20 \( \mu \)m. The pinholes are arranged in a spiral shape separated by 100 \( \mu \)m.
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Fig. 2.2. $I(z)$ as a function of the relative position of the focal $z$ for the objectives used:  $\cdot$ 10x, $\cdot$ 20x and $\cdot$ 50x (see Table 2.1 for details).

The rotating Nipkow disk is illuminated by means of a white light Xenon source and acts as a scanning multiple-point light source, which is imaged onto the object focal plane of the microscope objective. Each Nipkow pinhole acts as its own detector of the reflected light. After a reflection by the beam splitter, a CCD detector measures simultaneously the intensity for 512x512 pixels. This measurement is performed for every discrete step along the $z$ direction.

Fig. 2.2 shows $I(z)$ of the objectives used. A larger numerical aperture leads to a smaller FWHM and therefore a higher axial resolution. In Table 2.1 the specifications of the objectives are listed.

Table 2.1. Specifications of the microscope objectives used.

<table>
<thead>
<tr>
<th>Microscope objective</th>
<th>10x</th>
<th>20x</th>
<th>50x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Numerical aperture [-]</td>
<td>0.30</td>
<td>0.46</td>
<td>0.8</td>
</tr>
<tr>
<td>Working distance [mm]</td>
<td>10.1</td>
<td>3.1</td>
<td>0.66</td>
</tr>
<tr>
<td>Maximum surface slope according eq. (2.2) [°]</td>
<td>8.7</td>
<td>13.7</td>
<td>26.6</td>
</tr>
<tr>
<td>Measurement field [µm]</td>
<td>1450x1410</td>
<td>725x705</td>
<td>290x282</td>
</tr>
<tr>
<td>FWHM according eq. (2.1) ($\lambda = 500nm$) [µm]</td>
<td>19.1</td>
<td>7.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Axial resolution [nm]</td>
<td>50</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>Lateral resolution [µm]</td>
<td>2.83</td>
<td>1.42</td>
<td>0.57</td>
</tr>
</tbody>
</table>
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2.2.2 Calibration

Optical systems always show imperfections because perfect lenses do not exist. With a silicon wafer the parabolic shape of the lenses become visible. For height measurements these imperfections should be taken into account. In general a series of reference images at different positions is created using a silicon wafer as a calibration sample. The average of all these images will be subtracted from the measured data. Dust and other artifacts will degrade the average. Removal of the artifacts should be performed before the average is taken. The technique used is based on the removal of the point which deviates most from the average at each position \((x_i, y_j)\). From this new set of data points, the average is calculated. Subtracting this average from a confocal height image will remove the lens aberration from the measurement. In Fig. 2.3 an example of an averaged reference series is shown. The surface looks spherical, because the lenses have a spherical shape. From each measurement, the averaged reference series is subtracted.

![Image of averaged reference series](image)

Fig. 2.3. An averaged reference series for the 20x objective. The average is taken from a series of 5 images omitting the most deviating points compared with the average.

2.2.3 Surface characterization

Surfaces are in general rough and fractals comprise a useful statistical concept for the description of roughness. Fractals can be grouped in self-similar and self-affine. Self-similar stands for scale invariant i.e. the shape is similar on every scale. Typical examples were given by Mandelbrot [4]. Helge von Koch described the Koch island in 1904 [5]. Fractals are often made by recursion. In Fig. 2.4, the first recursive steps of the Koch islands are shown. Every side of the triangle is divided in 3 equal segments. From the centre segment a new triangle is drawn. After a few iterations a snowflake appears.
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Fig. 2.4. The Koch island in the first 3 iteration steps [6].

Self-affine surfaces are statistically invariant under the following rescaling: multiplication of the projected distance along the surface by a value $\varepsilon$; multiplication of the height by a different value $\varepsilon^{-H}$. Therefore, self-affine surfaces can be described by a single-valued self-affine function, which has the property

$$h(x, y) = \varepsilon^{xH_y} \cdot \varepsilon^{-H} h(x, x, y),\quad (2.5)$$

where $h(x, y)$ is the surface height at position $(x, y)$ and $H_x$ and $H_y$ are the so-called Hurst exponents along $x$ and $y$ respectively, usually $H_x = H_y = H_0$.

First-order statistics

One of the main characteristics is the surface height distribution function $p(h)$, where $p(h)dh$ is the probability of finding a surface height between $h$ and $h+dh$ at any point. By definition $\int_{-\infty}^{\infty} p(h)dh = 1$. The most general distribution is the so-called Gaussian height distribution (although originally proposed by Abraham de Moivre):

$$p(h) = \frac{1}{w \sqrt{2\pi}} e^{-\frac{h^2}{2w^2}}\quad (2.6)$$

In eq. (2.6) $w$ is the interface width or root-mean-square (rms) roughness of the surface. In general, it is more convenient to describe the surface by one or more parameters. A generalized method is to define the $n$-th order central moment

$$m_n = \int_{-\infty}^{\infty} (h-\overline{h})^n p(h)dh,\quad (2.7)$$

where $\overline{h}$ is the average surface height. The second order $m_2$ is equal to $w^2$. The third moment $m_3$ is related to the skewness of the surface height and is defined as

$$\gamma_1 = \frac{m_3}{w^3}.\quad (2.8)$$

The skewness is a measure of the symmetry of $p(h)$. The sign of the skewness reflects that the far off points are above or below the mean surface level $\overline{h}$. For example, a flat surface with dents will have a negative skewness.

Another important parameter is the kurtosis of the surface height.
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\[ \gamma_s = \frac{m_r}{w^4}. \]  \hspace{1cm} (2.9)

The kurtosis displays if a large amount of surface features is located far away from the mean surface level. A Gaussian distribution has a kurtosis equal to three.

**Second-order statistics**

The first order statistics cannot describe the statistical correlation of different points. It is quite possible to have very different surfaces with the same first-order statistics. Second-order statistics have to be used in that case. A common way is to express the average square height difference as a function of the lateral distance \( r \):

\[ g(r) = \langle (h(x+r) - h(x))^2 \rangle. \]  \hspace{1cm} (2.10)

In Table 2.2 examples of analytical descriptions of \( g(r) \) are shown for various types of surfaces. In all functions a lateral correlation length \( \xi \) [7] appears. Below \( \xi \) a scaling law applies, whereas above \( \xi \) first order statistics governs.

### Table 2.2. Surface types with the corresponding scaling functions \( \rho(r) \) below \( \xi \).

<table>
<thead>
<tr>
<th>Surface type (below ( \xi ))</th>
<th>Function ( \rho(r) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian</td>
<td>( \rho(r) = \exp\left(-\frac{r}{\xi}\right) )</td>
</tr>
<tr>
<td>Exponential</td>
<td>( \rho(r) = \exp\left(-\frac{r^2}{\xi^2}\right) )</td>
</tr>
<tr>
<td>Lorentzian</td>
<td>( \rho(r) = \xi^4 \left(\xi^2 + r^2\right)^{-1} )</td>
</tr>
<tr>
<td>Power-Law</td>
<td>( \rho(r) = \left(1 + r^2 / \xi^2\right)^{-\frac{1}{2}} )</td>
</tr>
<tr>
<td>Self-Affine</td>
<td>( \rho(r) = \exp\left(-\frac{r^2}{\xi^{2H}}\right) )</td>
</tr>
</tbody>
</table>

In Fig. 2.5 the curves associated with the expressions of Table 2.2 are displayed. For the self-affine surface, a third parameter \( H \) or Hurst exponent is defined. The correlation functions in Table 2.2 show that Gaussian (\( H = 1 \)) and exponential (\( H = \frac{1}{2} \)) surfaces are special cases of self-affine surfaces. The other curves can also be approximated by a self-affine curve with \( H = 1 \).

Fig. 2.6 shows three examples of line profiles with the same first order statistics \((w = 1, \, \gamma_3 = 0 \, \text{and} \, \chi_1 = 3)\), and equal correlation length \( \xi \). The three curves are illustrations of exponential (\( (H = \frac{1}{2}) \)), self-affine (\( H = 0.75 \)) and Gaussian surfaces (\( H = 1 \)). For fixed \( w \) and \( \xi \), a small value of \( H \) (e.g. 0.5) results in larger fluctuations on a short length scale than for large values of \( H \) (e.g. 1). Typical values for the Hurst exponent are between 0.5 and 1. In section 2.3.3, a plastically deformed metal will be described in terms of \( H \), \( \xi \) and \( w \).
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Fig. 2.5. Curves associated with the expressions in Table 2.2 with $\xi = 100$ and $H = 0.8$ on log-log scale.

Fig. 2.6. Examples of line-profiles with $\xi = 3.5$ for various Hurst exponents from top to bottom: 0.5, 0.75 and 1.

**Application of second order statistics**

From the surface height images $g(r)$ is estimated using a modification of eq. (2.10):

$$g_x(r) = \frac{1}{N_x(N_x - r)} \sum_{i=1}^{N_x} \sum_{j=r}^{N_x} [h(x_i + r, y_j) - h(x_i, y_j)]^2$$

(2.16)

and

$$g_y(r) = \frac{1}{N_y(N_y - r)} \sum_{j=1}^{N_y} \sum_{i=r}^{N_y} [h(x_i, y_j + r) - h(x_i, y_j)]^2,$$

(2.17)

where the height for each discrete location is defined as $h(x_i, y_j)$. The number of discrete points in both directions are denoted $N_x$ and $N_y$ respectively and $r$ is the distance between the points.

Eq. (2.16) is simply the average $g(r)$ determined from a number $N_x(N_x - r)$ measurements in the image. For large values of the distance $r$ the number of measurements involved in the average $g(r)$ becomes so low that a combination of several measurements is necessary to improve the precision.

The next step is to fit $g(r)$ to $g_x(r)$ by using eq. (2.15). If the correlation length $\xi$ is large enough, the slope of $g_x(r)$ in log-log space will be linear below $\xi$ and equal to $-2w^2 \rho(r)$. A linear least square fit of $g(r)$ to $g_x(r)$ will be in that case sufficient. The rms roughness amplitude $w$, or standard deviation of the surface height can be computed with the second moment of eq. (2.7) or from the $g_x(r)$:
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\[ w_i^2 = \frac{\sum_{r=4N_i}^{N_i} (N_i - r) g_i(r)}{2 \sum_{r=4N_i}^{N_i} (N_i - r)}. \] (2.18)

In eq. (2.18) the weighted average is taken from the long range \((r \gg \xi)\) values of \(g_i(r)\). Some surfaces show certain directionality e.g. texture, calculating \(w_i\) according to eq. (2.18) will incorporate this.

According to eq. (2.15), the correlation length \(\xi\) is defined as the point where the linear least square fit is equal to the long range value \(2w_i^2\).

Another way to determine the correlation length can be derived from eq. (2.15) by setting \(r = \xi\). The correlation length \(\xi\) will then be equal to the value of \(r\) where the following relation applies:

\[ g_i(r) = 2w_i^2(1 - e^{-r}). \] (2.19)

In Fig. 2.10 an example of the surface height is given. Applying the fit on \(g_i(r)\) of this surface results in the following curves (Fig. 2.7).

![Graph showing the function \(g_i(r)\) obtained for the surface shown in Fig. 2.10 expressed by \((\circ)\). Three lines are added showing the self-affine response for \(r \ll \xi\) and first order statistics for \(r \gg \xi\). The open square denotes \(\xi\) found using eq. (2.19) and the filled square the crossing of the self-affine response with the first order response (the other method).](image-url)
2.3 Basic physical concepts

2.3.1 Polymer
Polymers are built up from a large number of molecular units, which are linked together by weaker covalent bonds. Usually, the molecular units consist of e.g. carbon C, nitrogen N, oxygen O and halogens. In this thesis Poly(ethylene) Terephthalate (PET) will be used throughout. In Fig. 2.8 the schematic representation of the molecular unit, i.e. monomeric unit of PET, is shown. PET is produced industrially by either terephthalic acid or dimethyl terephthalate with ethylene glycol [9].

![Monomeric unit of PET](image)

Fig. 2.8. Monomeric unit of PET.

Crystallinity
PET is a semi-crystalline polymer, e.g. crystalline and amorphous phases coexist. The crystalline phase consists of lamellae [9]. Each lamella is built up of oriented polymer chains. The amorphous phase is by definition a state of disordered. Therefore the density of the amorphous phase is lower and the extra free volume makes it less resistant to chemicals.

The amount of crystalline phase is affected by the temperature treatment and the polymer characteristics e.g. chain length or side groups. Above the melting temperature $T_m$ the polymer is amorphous. Below the glass transition temperature $T_g$ the mobility of the polymer chains is so low that the crystalline fraction is fixed. During deformation, e.g. drawing, the crystallinity might increase [9].

In several applications amorphous polymers are desirable due to their mechanical and optical properties. In order to reach amorphous PET, the resin should be modified with approximately 30 % of the co-monomer cyclohexane dimethanol. This modification of PET is called PETG, because of the glycol side groups. In Table 2.3 a couple of specific properties of both polymers are shown. PETG will be used in various experiments. Nevertheless, both are shown in Table 2.3 to emphasize the similarity of both polymers.
Table 2.3. Selected material properties of PET and PETG [11,12].

<table>
<thead>
<tr>
<th>Material property</th>
<th>PET</th>
<th>PETG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic modulus $E$ [GPa]</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Glass transition temperature $T_g$ [°C]</td>
<td>63-79</td>
<td>75-80</td>
</tr>
<tr>
<td>Melting temperature $T_m$ [°C]</td>
<td>255</td>
<td>-</td>
</tr>
<tr>
<td>Density $\rho$ [g/m³]</td>
<td>1.4</td>
<td>1.27</td>
</tr>
<tr>
<td>Yield strength $\sigma_y$ [MPa]</td>
<td>~49</td>
<td>52</td>
</tr>
<tr>
<td>Strain at yield $\epsilon_y$ [%]</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Solvent</td>
<td>1,1,1,3,3,3 Hexafluoro-2-propanol</td>
<td>CHCl₃ (Chloroform)</td>
</tr>
</tbody>
</table>

Deformation

The mechanical and thermal properties of polymers are determined by the crystallinity, chain length, side groups and molecular bonds. For mainly amorphous PET or PETG the stress-strain curve can be grouped into four regions (see e.g. Fig. 2.16): visco-elastic (region I and II), softening (region III) and strain hardening (region IV). The nature of each of these regions will be summarized in the following [10]. Short-range, elastic deformations occur at small strains (region I) and involve bending, stretching, and small angular rotations of the network strands. With increasing stress, the chains are able to overcome the intermolecular resistance to rotation and shear. This is the beginning of yield (region II). Subsequently, “strain softening” follows where the flow stress decreases with increasing strain (region III). This instability is common to most glassy polymers and results in inhomogeneous yielding, which often leads directly to ductile failure. It is thought that strain softening results from shear-induced changes in the structure of the polymer. The strain softened regions are subject to larger local strains and strain rates than the un-yielded portions, frequently resulting in micro shear bands and shear patches. For sufficient large strains the network experiences large scale changes in chain conformation and begins to orient parallel to the tensile direction or perpendicular to the compression axis, thus producing a macroscopically anisotropic material. In region IV, strain hardening stabilizes the softened regions.

Sample preparation using spin-coating

Spin-coating is a common technique for depositing thin layers from solution. A metal substrate is wetted completely with a solution of PETG in chloroform. Immediately after wetting the sample is rotated at a certain speed. Due to the rotation, a mayor part of the solution is removed. The rotation also causes fast evaporation of the solvent. The final thickness depends on the solution viscosity, the rotation speed, the evaporation rate and
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the wettability of the substrate. In our experiments we choose to keep the rotation speed constant at 120 rpm. The thickness is therefore determined by the viscosity of the solution. The viscosity of the solution is varied by the weight percentage of PETG. Sample thicknesses from 2 µm to 15 µm can be obtained for solutions with 2wt% to 12wt% PETG. In order to obtain coatings with a larger thickness the spin coating process is repeated. The thickness was measured with a confocal microscope after removing the coating locally with a laser [13]. For transparent films a profilometer was used. For white coatings, the confocal microscope can also be used. The thickness of the coating is determined by the height difference between the uncoated and coated part. To get a good estimate of the thickness, the average is taken of at least 10 positions.

2.3.2 Mechanisms of roughening

Macroscopic homogenous plastic deformation leads to inhomogeneous deformation of the material. The inhomogeneous deformation can be grouped in different scales: Sample size, grain size or within grains. The plastic straining of polycrystalline metals is accompanied by a gradual development of microstructural surface defects.

During plastic deformation several mechanisms appear. One of them is inhomogeneous plastic deformation on a sample size and an example is the effect of Lüders bands in the body-centered cubic (bcc) structure [14]. On the grain size scale, orange peel originates from interaction between individual grains and is often seen at the surface by out-of plane displacements of grains. Within the grain, different dislocation mechanisms may act as a result of the applied displacements. Surface twins occur when a grain experiences a homogeneous shear when a limited number of slip systems is active. Slip-bands become visible as atomic steps at the outer surface.

The various mechanisms can be distinguished using confocal microscopy. Fig. 2.9 shows the reflected image of the metal surface, where the whole surface is in focus. The

![Fig. 2.9. Reflection measurement of rough fcc steel (number average grainsize 8 µm).](image1)

![Fig. 2.10. Surface height of the surface in Fig. 2.9.](image2)
Slip bands are small steps at the surface. In reflection the mode these steps are clearly visible. The surface height can also be displayed (Fig. 2.10). An example of orange peel is the rotated grain in Fig. 2.9 (fcc steel). A probable twin is shown in Fig. 2.9, but examples of twins can be found in Fig. 2.11.

2.3.3 Statistics of roughening

In this section, the surface roughness as a function of strain is analyzed for an austenitic (fcc) steel. The as-received steel is polished prior to the deformation process. An example of the surface roughness after deformation is shown in Fig. 2.10. In Fig. 2.11a, electron back scattered diffraction (EBSD) is used to determine the grain boundaries in the material under investigation. About 30% of the boundaries are twin boundaries (misorientation angle of 60 degrees). In Fig. 2.11b the distribution of the grain size is shown. The number average grain size is $8\mu m$, including twin boundaries. The distribution of the orientation in Fig. 2.11c shows a certain texture.
In Fig. 2.12a $g,(r)$ for two objectives are shown. Each curve is the average of 3 confocal measurements. For each strain the experiment with two objectives (20x and 50x) show a similar saturation $2w^2$. In Fig. 2.12b the rms roughness amplitude $w_r$ as a function of the strain $\varepsilon$ is shown. The error bars show the difference between measurements performed with different objectives. The phenomenological relationship between $\varepsilon$ and $w_r$ can be written as follows:

$$w_r(\varepsilon) = c_1 \left(1 - \exp\left[c_2 \varepsilon\right]\right), \quad (2.20)$$

where $c_1$ is the saturation value of the roughness and $c_2$ is the negative constant which determines the slope of the curve. Eq. (2.20) describes a linear roughening response [15,16], but also the behavior shown in Fig. 2.12b [15,17]. The slope of the curve at $\varepsilon = 0$ is given by differentiating (2.20):

$$\frac{d w_r(\varepsilon)}{d \varepsilon} \bigg|_{0} = -c_1 c_2 \exp[c_2 \varepsilon] \bigg|_{0} = -c_1 c_2. \quad (2.21)$$

In Fig. 2.12a the slope of the different curves looks similar below the correlation length $\xi$. The slope is shown in terms of the Hurst exponent $H$ in Fig. 2.13. Fig. 2.14 shows $\xi$ as a function of the strain. For low magnification, the resolution of the confocal microscope is not sufficient to characterize polished surfaces (Table 2.1). Therefore, the $H$ and $\xi$ can only be calculated for larger strains. The Hurst exponent saturates at $H = 0.87 \pm 0.05$ and the correlation length saturates at $\xi = 55 \pm 10 \mu m$. 

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A summary of the self-affine characteristics is presented in Table 2.4 for a selection of materials. In chapter 5, a more detailed description will be presented.

### Table 2.4: Self-affine surface evolution characteristics of a few selected materials [18,19,20].

<table>
<thead>
<tr>
<th></th>
<th>Iron</th>
<th>Steel</th>
<th>Steel (Fig. 2.9-Fig. 2.14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>BCC</td>
<td>BCC</td>
<td>FCC</td>
</tr>
<tr>
<td>Thickness [nm]</td>
<td>1.5</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Grain size [µm]</td>
<td>153</td>
<td>12</td>
<td>8 or 15 (excluding twins)</td>
</tr>
<tr>
<td>Hurst exponent [-]</td>
<td>0.69 ± 0.05</td>
<td>0.72 ± 0.05</td>
<td>0.87 ± 0.05</td>
</tr>
<tr>
<td>Correlation length [µm]</td>
<td>250 ± 25</td>
<td>38 ± 7</td>
<td>55 ± 10</td>
</tr>
<tr>
<td>Slope of ( w_r(0) ) from eq. (2.21) [µm]</td>
<td>163</td>
<td>7.4</td>
<td>12.7</td>
</tr>
</tbody>
</table>

#### 2.3.4 Adhesion

Several attractions exist resulting in adhesion between two bodies: Interatomic and intermolecular. The strongest bonds are interatomic bonds. This group consists of ionic bonds, covalent bonds, metallic bonds and hydrogen bonds. The weakest bonds are intermolecular bonds. This group of bonds can be divided in dipole-dipole (excluding hydrogen bonds), London (dispersion) bonds and dipole-induced dipole bonds. Polymer-metal adhesion is primary based on: ionic bonds and hydrogen bonds. A short description of each bond type will follow [12,21].

**Ionic bond**

Ionic bonds are a type of chemical bond based on electrostatic forces between two oppositely-charged ions. In ionic bond formation, a metal donates an electron, due to a low electro negativity to form a positive ion or cation. In ordinary table salt, the bonds
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between the sodium and chlorine ions are ionic bonds. Often ionic bonds form between metals and non-metals. The non-metal atom has an electron configuration just short of a noble gas structure. They are electronegative, and so readily gain electrons to form negative ions or anions. The two or more ions are then attracted to each other by electrostatic forces. Such bonds are stronger than hydrogen bonds, but similar in strength to covalent bonds.

Hydrogen bond

A hydrogen bond is a type of attractive intermolecular force that exists between two partial electric charges of opposite polarity. Although stronger than most other intermolecular forces, the typical hydrogen bond is much weaker than both the ionic bond and the covalent bond.

As the name "hydrogen bond" implies, one part of the bond involves a hydrogen atom. The hydrogen atom must be attached to one of the elements oxygen, nitrogen or fluorine, all of which are strongly electronegative hetero atoms. These bonding elements are known as the hydrogen-bond donor. This electronegative element attracts the electron cloud from around the hydrogen nucleus and, by decentralizing the cloud, leaves the atom with a positive partial charge. Because of the small size of hydrogen relative to other atoms and molecules, the resulting charge, though only partial, nevertheless represents a large charge density. A hydrogen bond results when this strong positive charge density attracts a lone pair of electrons on another heteroatom, which becomes the hydrogen-bond acceptor.

Surface area

In general, an increase of the number of bonds yields to stronger adhesion. This can be achieved by increasing the surface area by roughening the interface. Roughening of the surface may also result in mechanical interlocking (Fig. 2.15), which makes the bodies to stick to each other even better.

The strength of adhesion can be measured by means of over 350 different techniques [22]. Nearly all techniques are based on interface fracture. In a couple of tests, the result is the work of adhesion \( G_0 \). For a metal \((m)\) and a polymer \((p)\) coming into contact per unit area the work of adhesion \( G_0 \) is defined as:

\[
G_0 = \gamma_m + \gamma_p - 2\gamma_{mp},
\]

(2.22)

where \( \gamma_m \) and \( \gamma_p \) represent the surface energies of the metal and the polymer and \( \gamma_{mp} \) is the interface energy.
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Fig. 2.15. Schematic of mechanical interlocking [23].

2.4 Numerical techniques

2.4.1 Introduction to continuum mechanics

The geometries used throughout this thesis can be simplified by a system consisting of two materials with an interface in between. External displacements or forces determine the deformation of the materials and the interface. This laminate can be analyzed numerically by means of a finite strain, finite element method [24,25]. It uses a Total Lagrangian formulation in which equilibrium is expressed in terms of the principle of virtual work as

$$\int \int \int \int \int \sigma_{ij} \delta \varepsilon_{ij} dV - \int \int \sigma_{ij} \delta u_{ij} dS = \int \int T_{ext} \delta u_{ij} dS .$$

(2.23)

The first integral contains the bulk materials. The second integral contains the interfaces in the laminate and the last integral contains the boundary conditions. In eq. (2.23) $\varepsilon_{ij}$ and $\sigma_{ij}$ are the components of the stress and strain tensor, respectively; $\delta$ is an weighting function for the variable appearing next to $\delta$ in eq. (2.23)[26]; $\sigma_{ij}$ are the interface tractions (see section 2.4.2); $\Delta_{ij}$ are the interface displacements; $T_{ext}$ is the surface traction and $u_{ij}$ are the surface displacements.

For small strains the relationship between the displacements $u_{ij}$ and the strain $\varepsilon_{ij}$ is given by

$$\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right).$$

(2.24)

The stresses can be expressed as a function of the stiffness tensor $C_{ijkl}$ and the strain:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl}. $$

(2.25)

The stiffness tensor incorporates the material properties e.g. Poisson’s ratio and elastic modulus. To incorporate plastic deformation in the material response, it is necessary to alter the stiffness matrix for every small displacement. This results in solving eq. (2.23) for every small step. The constitutive law describing the stress-strain characteristics of
the polymer is given in [27]. The parameters used are shown in Table 2.5. The corresponding stress-strain curve is presented in Fig. 2.16.

Table 2.5. Summary of the used material parameters of the utilized material model throughout this thesis [27].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E/s_0$</td>
<td>7.76</td>
</tr>
<tr>
<td>$s_{\alpha}/s_0$</td>
<td>0.774</td>
</tr>
<tr>
<td>$A_0/T$</td>
<td>91.99</td>
</tr>
<tr>
<td>$h/s_0$</td>
<td>3.9</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.25</td>
</tr>
<tr>
<td>$N$</td>
<td>12.602</td>
</tr>
<tr>
<td>$C^s/s_0$</td>
<td>0.132</td>
</tr>
</tbody>
</table>

Fig. 2.16. The engineering stress-strain response of the deployed material model, which represents PETG.

2.4.2 Cohesive surfaces

To incorporate failure of the interface, the method of cohesive surfaces is adopted. Rose et al. defined the first cohesive law [28]. This law was based only on separation perpendicular to the interface. The cohesive law used here, couples perpendicular or normal $\Delta_n$ and shear or tangential separation $\Delta_t$ [29].

In Fig. 2.17 two material bodies are shown. The interaction between the two bodies is controlled by the cohesive element. The tractions are determined by the energy potential $\Phi$ and the displacements $\Delta_n$ and $\Delta_t$ as
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\[ \sigma_n(\Delta_n, \Delta_t) = -\frac{\partial \Phi}{\partial \Delta_n} \quad \text{and} \quad \sigma_t(\Delta_n, \Delta_t) = -\frac{\partial \Phi}{\partial \Delta_t}. \] (2.26)

The potential \( \Phi \) is defined by

\[ \Phi = \sigma_n^{\text{max}} \Delta_n e \left( 1 - e^{-\Delta_n/\Delta_0} \right) \left[ 1 - r + \frac{\Delta_n}{\Delta_0} \left( \frac{1}{r} - 1 \right) \left( \frac{r - q \Delta_n}{r - 1} \right) e^{-\Delta_t^2/(\Delta_t^{\text{max}})^2} \right] \] (2.27)

and

\[ \Phi = \Phi_n + \Phi_t, \] (2.28)

where \( \Phi_n \) is the work of normal separation, \( \Phi_t \) is the work of tangential separation, \( \sigma_n^{\text{max}} \) is the maximum stress reached for pure opening, \( \Delta_0 \) is the normal separation at \( \sigma_n^{\text{max}} \), \( \frac{1}{2} \sqrt{2} \Delta_t^{\text{max}} \) is the tangential separation at maximum tangential traction \( \tau_t^{\text{max}} \). The parameters \( q \) and \( r \) govern the coupling between the normal and tangential response:

\[ q = \frac{\tau_t^{\text{max}} \Delta_t^{\text{max}}}{\sigma_n^{\text{max}} \Delta_n \sqrt{2} e} \quad \text{and} \quad r = \frac{\Delta_n}{\Delta_0} \] (2.29)

In general \( r \) and \( q \) are in the range of 0 to 1. Fig. 2.18a shows an example of the stress-displacement curve. Fig. 2.18b shows the energy as the area under the stress-displacement curve for the curve of Fig. 2.18a. The curve in Fig. 2.18a is the result of the calculation using eq. (2.26):

\[ \sigma_n(\Delta_n, \Delta_t) = \sigma_n^{\text{max}} e^{1-\Delta_n/\Delta_0} \left[ \frac{\Delta_n}{\Delta_0} e^{-\Delta_t^2/(\Delta_t^{\text{max}})^2} + \frac{1-q}{r-1} \left( \frac{r - q \Delta_n}{r - 1} \right) e^{-\Delta_t^2/(\Delta_t^{\text{max}})^2} \right] \] (2.30)

and

\[ \sigma_t(\Delta_n, \Delta_t) = 2 \left( \frac{\Delta_0 \Delta_t}{\Delta_t^{\text{max}}} \right) \sigma_n^{\text{max}} \left( q + \frac{r - q \Delta_n}{r - 1} \right) e^{1-\Delta_n/\Delta_0 - \Delta_t^2/(\Delta_t^{\text{max}})^2}. \] (2.31)

Examples are shown in Fig. 2.19 for eq. (2.30). The coupling between the normal and tangential tractions is visible: an increase of the tangential separation leads to a decrease of the maximum normal traction. The opposite effect is shown in Fig. 2.20 for the tangential tractions.

So far the coupling parameters \( q \) and \( r \) have been held constant and equal to each other. In Fig. 2.21 the effect of different values for \( q \) and \( r \) is shown. It is physically reasonable that the tangential tractions increase during normal compression. Furthermore, it is physically reasonable that for increasing normal displacement the tangential traction decreases. Both arguments are only satisfied when \( r = q \). In Fig. 2.22
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The effect of the parameter \( q \) on the normal traction is shown. In the case of a high \( q \) (e.g. 0.95) it is reasonable that failure of the element occurs by shear, whereas a low value of \( q \) will result mainly in normal displacements.

The definition of failure is ambiguous. From energetic point of view, the cohesive surface will be broken if the energy in the cohesive surface has reached the maximum value. But from stability point of view, the cohesive surface will be unstable if the maximum traction value is reached. At the maximum traction value, assuming normal opening, only 27\% of the total energy is dissipated (see Fig. 2.18).

---

![Fig. 2.19. Normalized normal traction as a function of the normalized normal separation for different tangential separations (\( r = q = 0.95 \))](image1)

\[ \Delta_n / \Delta_n^{\text{max}} = 0 \text{ (top), } 1 \text{ and } \infty \text{ (bottom).} \]

![Fig. 2.20. Normalized tangential traction as a function of the normalized tangential separation for different normal separations (\( r = q = 0.95 \))](image2)

\[ \Delta_t / \Delta_t^{\text{max}} = 0 \text{ (top), } 1 \text{ and } \infty \text{ (bottom).} \]

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![Fig. 2.21. The maximum normalized tangential traction as a function of the normalized normal separation for different \( r - q \) values: \(-0.2\), 0 and 0.2.](image3)

![Fig. 2.22. The maximum normalized normal traction as a function of the normalized tangential separation for different \( q \) values: 0.05(top), 0.275, 0.5, 0.725 and 0.95(bottom).](image4)
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2.4.3 Surface roughness implementation

Surfaces were created with a modified version of the Voss algorithm [30]. The Voss algorithm is based on the assumption that the statistics on all length scales are the same. This implicates the absence of a correlation length. In this algorithm, points which are located some distance $r$ apart, are given random displacement chosen from a Gaussian distribution with standard deviation of $w$. The points that moved are connected by straight lines. The remaining points are placed on these lines (Fig. 2.23).

For each refinement step the distance $r$ is divided by 2 and the standard deviation of the Gaussian distribution from which the displacements are chosen, is reduced according to the following equation:

$$w_i = w_0 \ell^{2H_i} \text{ with } i = 1, 2, \ldots, \log(N - 1).$$  

(2.32)

Here, $i$ is the refinement step number, $H$ the Hurst exponent, $\ell$ the scale factor or lacunarity (normally 0.5), $w_0$ the initial roughness amplitude and $N$ is the total number of points of the final surface. This algorithm is also tractable in more dimensions, but here for the sake of simplicity the algorithm is carried out for a 1D system.

Unfortunately the algorithm as such is not able to generate surfaces with specific topological properties. We are interested in an algorithm that is able to generate surfaces as a function of: the number of surface points $N$, the rms roughness amplitude $w$, the correlation length $\xi$ and the Hurst exponent $H$. In order to generate these surfaces we have chosen to adjust the amplitude $w_i$ of each refining step such that the generated rough surface obeys the predefined parameters. An easy way to express these values is with a function as shown in eq. (2.10). Self-affine surfaces can be described by eq. (2.15) [31]:

Fig. 2.23. Refinement algorithm used by R.F. Voss ($N = 9, w_0 = 1, H = 1$ and $\lambda = 0.5$): . first step; -- second step; - final surface.
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\[ g(r) = 2w^2 \left(1 - \exp[-(r/\xi)^{2H}]\right) \text{ with } 0 < H < 1. \]  

(2.33)

In fact, eqs. (2.10) and (2.15) are equal to each other except that eq. (2.10) describes a discrete case and eq. (2.15) describes the continuum case. Because the final surface \( g(r) \) is known (eq. (2.15)), it is important to know how each refinement step contributes to the final surface \( h(r) \). It is clear that the addition of two fully Gaussian random surfaces results in a \( g(r) \) function that is equal to the sum of contributing \( g(r) \) functions. For a finite number of points \( N \), the total \( g(r) \) for all Voss additions becomes:

\[ g(r) = \sum_{i=1}^{\log(N-1)} g_i(r) \]  

(2.34)

In Fig. 2.24 the \( g_i(r) \) functions of each refinement step is shown. In this figure only \( N \) and the refinement step determine the shape of the curves. For all these curves the initial standard deviation \( w_i \) is set to 1.

Fig. 2.24. Each Voss refinement step for a surface with 1025 points and initial rms roughness \( w_i = 1 \) according to eq. (2.39). The interpolation of the random distributed points leads to the small deviation at the right of the graph.

With introduction of an amplitude \( w_i \) for each curve, the sum of all these curves (eq. (2.34)) will produce \( g(r) \) that depends on the amplitude of each curve. By describing \( g(r) \), the problem of generating self-affine surfaces becomes the problem of finding the right amplitude \( w_i \) of each refinement step.

The squared height difference of two neighboring points is:

\[ g_i(l) = \frac{2w_i^2}{d_i^2} = \frac{2^{2i+1}w_i^2}{(N-1)^2} \]  

(2.35)
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where the distance between two displaced points is equal to:

\[ d_i = \frac{N - 1}{2^i} \]. \hspace{1cm} (2.36)

Due to the extrapolation, the actual standard deviation \( \sigma_{\text{actual}} \) will be less than the initial standard deviation (Fig. 2.24) and this will influence eq. (2.34). For a fully Gaussian surface the Hurst exponent \( H \) is equal to 1 and the lateral correlation length becomes:

\[
\xi_i = \frac{1}{\sqrt{-\log\left(1 - \frac{w_i^2}{d_i^2 \sigma_{\text{actual}}^2}\right)}} = \frac{1}{\sqrt{-\log\left(1 - \frac{4 w_i^2}{(N-1)^2 \sigma_{\text{actual}}^2}\right)}} \hspace{1cm} (2.37)
\]

The ratio of the initial standard deviation \( w_i \) and the actual standard deviation \( \sigma_{\text{actual}} \) can be written as a function of the refinement step \( i \) and the surface size \( N \):

\[
\frac{\sigma_{\text{actual}}^2}{w_i^2} = \frac{1}{d_i} \sum_{j \neq i} \left(1 - \frac{j}{d_i}\right)^2 + \left(\frac{i}{d_i}\right)^2 = \frac{1}{3} \left(2 + \frac{4^i}{(N-1)^2}\right). \hspace{1cm} (2.38)
\]

Taking eqs. (2.15), (2.37) and (2.38) together, the \( g_i(r) \) of one added Voss surface can be described by only three parameters: the rms surface roughness \( w_i \), the surface size \( N \) and the refinement step \( i \):

\[
g_i(r) = 2 \sigma_{\text{actual}}^2 \left(1 - e^{-\left(\frac{r}{\xi_i}\right)^2}\right) = \frac{2}{3} \left(2 + \frac{4^i}{(N-1)^2}\right) \left(1 - \frac{6(N-1)^2}{4^i + 2(N-1)^2 - 2}\right)^{\frac{r^2}{2}} w_i^2. \hspace{1cm} (2.39)
\]

By calculating the \( g_i(r) \) for several distances \( r \), it is possible to generate a set of linear equations of the form:

\[ 2 \cdot A \cdot w_i^2 = g(r). \hspace{1cm} (2.40) \]

In eq. (2.40) \( g(r) \) is defined by eq. (2.15) and the square matrix \( A \) is defined by:

\[
A(r,i) = \frac{1}{3} \left(2 + \frac{4^i}{(N-1)^2}\right) \left(1 - \frac{6(N-1)^2}{4^i + 2(N-1)^2 - 2}\right)^{\frac{r^2}{2}} \hspace{1cm} (2.41)
\]

According to eq. (2.40) and eq. (2.41) it is important to choose the distances \( r \) with great care. \( g(r) \) is an exponential function and the distance between two points also shows a power function of the refinement step. Both arguments yield the distances \( r \):

\[ r_j = 2^j - 1 \text{ with } j = 1, 2, \ldots, 2 \log(N-1) \hspace{1cm} (2.42) \]
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The refinement step \( i \) covers the same range of values as \( j \). Combining eq. (2.41) and (2.42) we are able to generate the square matrix \( A \) for a given number of surface points \( N \). If the square matrix \( A \) is non-singular, there is a unique solution of eq. (2.40). This solution might contain negative values \( (w_i^2 < 0) \), which cause an imaginary surface. The only way to tackle this problem is to find a solution that is very close to eq. (2.40) with only non-negative \( w_i^2 \) values. For this problem several solutions are available [32, 33, 34].

By solving eq. (2.40) for a given number of surface points, correlation length, Hurst exponent and rms roughness amplitude, we are able to generate the coefficients \( w_i \) for the Voss algorithm. Some examples of calculated surfaces are given in Fig. 2.6 and Fig. 2.25.

![Fig. 2.25. Three examples of calculated surfaces for the following parameters: \( N = 1025 \), \( w = 1 \), \( \xi = 35 \) and \( H = 0.3 \) (left), 0.6 (middle) and 0.9 (right).](image)

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