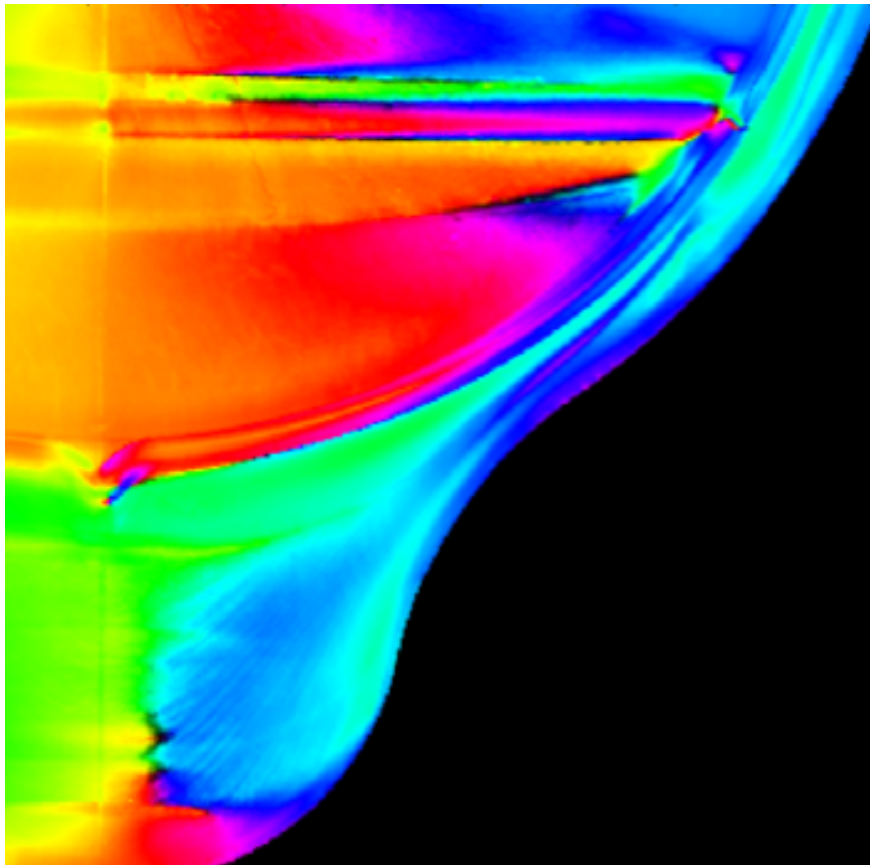




CHALMERS
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Characterisation of Injection Moulded Polymer Materials using SAXS and WAXS

Master's thesis in Applied Physics

LINNEA BJÖRN

MASTER'S THESIS 2018

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LINNEA BJÖRN



Department of Physics
Division of Condensed Matter Physics
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2018

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Supervisors: Marianne Liebi, Department of Condensed Matter Physics, Chalmers
University of Technology,
Elin Persson Jutemar, Tetra Pak
Eskil Andreasson, Tetra pak
Examiner: Marianne Liebi, Department of Condensed Matter Physics, Chalmers
University of Technology

Master's Thesis 2018
Department of Physics
Division of Condensed Matter Physics
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

Cover: Scanning SAXS of a commercially available opening device at Tetra Pak®
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Abstract

Investigation of the microstructure of polymer materials has been of interest in the recent decades since it defines the mechanical properties of the material. For many commercial applications, understanding the microstructure is key in order to prevent failure and increase quality of the material. This information can also be used to evaluate and modify existing materials and/or design new materials. At Tetra Pak®, packaging solutions for food are constantly developed and improved in order to meet customer's needs. A long-term goal of the company is to include detailed material structures into their virtual simulations and thus predict mechanical properties with improved accuracy. Polymers are often anisotropic materials of which properties are highly effected by processing conditions and can therefore be difficult to predict.

In this master's thesis, Small and Wide Angle X-ray Scattering (SAXS and WAXS) at both laboratory and synchrotron X-ray sources has been used to study the structure of some semicrystalline polymers used at Tetra Pak® at several different length scales. The scattering data showed that there are several different types of microstructures present in the sample resulting in a layered structure of the material. It was also shown that the microstructure was highly effected both by the position in the sample measured and viscosity of the polymer used. Furthermore, by combining the results from scanning SAXS/WAXS and tensile testing, some links could be established between the material morphology and the mechanical performance of the material.

Keywords: Scanning SAXS/WAXS, Injection moulded polymer, LDPE

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Contents

List of Figures	xi
List of Tables	xii
List of Aberrations	xiii
1 Introduction	1
1.1 Aim	2
1.2 Limitations	2
1.3 Scientific Context	2
2 Theory	3
2.1 Introduction to Crystal Lattice	3
2.2 Polymers	6
2.2.1 Crystalline Phase of Polymers	6
2.2.2 Hierarchic Structure of Polymers	7
2.2.3 Mechanical Behaviour of Polymers	8
2.2.4 Polyethylene	9
2.3 Injection Moulding of Polymers	10
2.4 X-ray Scattering	12
2.4.1 X-ray Scattering of Polyethylene	14
2.5 Scanning Electron Microscopy	14
3 Experimental Methods	15
3.1 Material	15
3.2 Sample Preparation	16
3.3 X-ray Diffraction Experimental Setup	19
3.4 Processing and Interpretation of Scattering Data	20
4 Results and Discussion	23
4.1 Quantifying the Diffraction Signal of PE	23
4.2 Preliminary Studies at CMAL	25
4.3 Scanning SAXS and WAXS of Test Plates	28
4.4 Scanning SAXS of Deformed Samples	35
4.5 Mechanical Properties	38
4.6 Scanning SAXS of Commercially Available Products	39
4.7 SEM of Deformed Samples	41

5	Conclusions	43
6	Future Work	45
	Bibliography	47

List of Figures

2.1	An example of a Bravais lattice where the unit cell is shown in green. a , b and c are the basis vectors of the unit cell and T is the translation vector by which one can move one lattice point to another [1].	3
2.2	Example of Miller indices for different planes of a simple cubic lattice.	4
2.3	Example of crystal planes with corresponding interplanar spacings [1].	5
2.4	Polymer architectures.	6
2.5	The semicrystalline structure of a linear polymer. d_c is the thickness of a crystalline lamella, d_a is the thickness of the amorphous layer and d_{ac} is the thickness of one lamella and one amorphous region [2].	7
2.6	Hierarchic structures that semi crystalline polymers may form.	7
2.7	A typical stress-strain curve for a semicrystalline polymer.	8
2.8	The chemical formula of polyethylene.	9
2.9	The unit cell of orthorhombic polyethylene.	9
2.10	The characteristic flow pattern of injection moulding.	10
2.11	The shear rate profile in fountain flow [3].	11
2.12	Layers in injection moulded polymer plate.	11
2.13	The experimental setup of SAXS/WAXS.	12
2.14	X-rays scattering on two neighbouring atom planes.	13
3.1	Dimensions of the injection moulded test plate.	16
3.2	Preparation of samples from test plate.	17
3.3	Preparation of dogbone-shaped samples for tensile testing.	17
3.4	Side view and top view.	18
3.5	X-ray scattering pattern and radially integrated data averaged for sectors 1 and 2 as indicated in the scattering pattern.	21
3.6	X-ray scattering pattern and azimuthal intensity distribution plot averaged for the q -region indicated in the scattering pattern.	21
4.1	Diffraction pattern of the bulk layer of medium viscosity LDPE, taken in side view. The SAXS signal is shown in blue and the WAXS signal is shown in red.	23
4.2	Radially integrated SAXS data for four different positions a, b, c and, d of a medium viscosity LDPE test plate.	25
4.3	WAXS result for a sample deformed in CD. The position of the three points measured is shown together with the raw- and radially integrated data from each point.	26

4.4	WAXS result for a sample deformed in MD. The position of the three points measured is shown together with the raw- and radially integrated data from each point.	27
4.5	Visualisation of the layered structure of medium viscosity LDPE by using (a) polarised light optical microscopy for sample a without pigment, (b) scanning SAXS symmetric amplitude for a sample without pigment and c) scanning SAXS symmetric amplitude for a sample with pigment	29
4.6	Symmetric amplitude with scattering patterns for some selected areas, degree of orientation and asymmetric amplitude for medium viscosity LDPE at position CD2 and MD.	30
4.7	The proposed microstructure of injection moulded polyethylene. . . .	31
4.8	Symmetric amplitude plots taken at CD1, CD2 and CD3.	32
4.9	Comparison between the scanning SAXS plots of low and medium viscosity LDPE.	33
4.10	Symmetric Amplitude plot of pigmented medium viscosity LDPE. . .	34
4.11	Scanning SAXS of a medium viscosity LDPE dogbone deformed in the CD2 direction.	35
4.12	The proposed microstructure, before and after deformation in CD. The red arrows indicate the direction of the applied force.	36
4.13	Scanning SAXS of a medium viscosity LDPE dogbone deformed in the CD2 direction.	36
4.14	The proposed microstructure, before and after deformation in MD. The red arrows indicate the direction of the applied force, and the black stripes indicate the cracking of the shish-kebab microstructure.	37
4.15	Tensile test of LDPE with different viscosities. The solid line represents the average stress/strain curve of 10 samples. The break point for each sample is shown as dots.	38
4.16	Scanning SAXS of a commercially available opening device for pigmented medium viscosity LDPE.	40
4.17	SEM images of a sample deformed in MD.	41

List of Tables

3.1	The experimental parameters for the SAXS and WAXS configurations for the measurements performed at CMAL and PSI.	20
4.1	Characterisation of the diffraction peaks of PE. The table summarises the q -value, the calculated d -value, the crystal plane and the theoretical d -value for each peak.	24

List of Abberrations

CD	Cross Direction
CMAL	Chalmers Materials Analysis Laboratory
CXS	Coherent X-ray Scattering
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
LOM	Light Optical Microscopy
MD	Machine Direction
PSI	Paul Scherrer Institut
SAXS	Small Angle X-ray Scattering
SEM	Scanning Electron Microscopy
SLS	Swiss Lightsource
WAXS	Wide Angle X-ray Scattering
XRD	X-ray Diffraction

1

Introduction

Polymers are widely used materials found almost everywhere in our daily life. The applications of polymers range from constructing materials to fabrics and different polymers exhibit very different material properties. Not only is it difficult to imagine modern society without man-made polymers, but natural polymers such as DNA and proteins are fundamental building blocks for the cells of all life on Earth. Thus, investigation, development and optimisation of polymer materials are all of great importance.

One important usage of polymers is liquid food packaging, and Tetra Pak® is the world's leading company in the field. At Tetra Pak®, injection moulding is a commonly used processing technique for polymers. Previous work has shown that during injection moulding the polymer chains often align in the direction of the melt flow, resulting in strongly anisotropic materials with different mechanical properties in different directions [4]. Macroscopic material properties, such as mechanical behaviour, are defined by the microstructure of the material. Hence, to understand the observed anisotropic material properties further, detailed knowledge of the microstructure is needed. Important features in the microstructure include the direction of the crystalline regions, crystallinity and the thickness and size distribution of the crystal lamellae. A long term goal at Tetra Pak is to use these detailed material characteristics as input for their virtual simulations. By doing so they can with improved accuracy predict material properties and thus reduce the number of physical tests needed. This may result in reduced cost and material usage of their commercially available products.

Furthermore, previous work at Tetra Pak® has shown that their injection moulded parts not only have different material properties in different positions of the sample, but also have varying microstructure throughout the thickness of the material. By using Light Optical Microscopy (LOM), a layered material structure has been observed. In order to use LOM, the sample needs to be transparent. However, most polymers that are used in commercial products from Tetra Pak® contain pigment and thus other techniques are needed in order to investigate the corresponding microstructure in these samples. In addition, LOM can only be used to visualise different layers but does not give any information about the structure within each layer.

1.1 Aim

The aim of this master's thesis is to investigate the possibilities and opportunities to use small- and wide angle X-ray scattering (SAXS and WAXS) for characterisation of injection moulded polymer parts, i.e. tops or closures from Tetra Pak®. By using scanning SAXS/WAXS the objective is to determine microstructure of injection moulded polymers through extended areas. Apart from doing SAXS/WAXS measurements, the ambition is to use complementary techniques, such as tensile testing and SEM analysis, in order to link the material morphology created during the manufacturing process to the mechanical performance of the material.

1.2 Limitations

The focus of the project will be kept to analysing the microstructure of polymer material rather than optimising the microstructure by changing processing parameters. The aim is not to do a full parameter study, but rather focus on demonstrating the capabilities of SAXS/WAXS, and in particular scanning SAXS/WAXS for some selected injection moulded polymers.

1.3 Scientific Context

Since the mechanical performance of a polymer is highly dependent on its microstructure, many studies have been carried out investigating how various processing parameters, such as flow, shear rate, molecular weight of the polymer, stress overshoot and more, influence the microstructure of different polymers [5, 6, 7, 8]. Furthermore, as injection moulding is one of the most commonly used processing technique for polymers in varying applications, several studies have been reported focusing exclusively on the microstructure in injection moulding polymers [9, 10, 11, 12, 13]. In these studies diverse experimental techniques are reported, where some of the most common ones are optical microscopy [9, 12] and point measurements of SAXS and WAXS [9, 5, 12]. However, no previous studies have been found that uses scanning SAXS/WAXS in order to investigate the layered structure of injection moulded polymers through extended areas.

2

Theory

2.1 Introduction to Crystal Lattice

In an ideal crystal the atoms have well defined positions and are evenly spaced from each other in three infinite directions in space. In reality this is clearly not the case, and the regularity must eventually be interrupted since the crystals are finite in size. In addition, other defects are most often included in the crystal. However, the strict description of an ideal crystal is still of importance for the understanding of X-ray diffraction. [1]

An ideal crystal can mathematically be described as an infinite regular lattice of points where each point can be reached by the translation vector $\mathbf{T}$.

$$\mathbf{T} = u_1\mathbf{a} + u_2\mathbf{b} + u_3\mathbf{c} \quad (2.1)$$

where u_1 , u_2 and u_3 are integers and $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are basis vectors. A lattice that can be described by this equation is called a Bravais lattice and the length of the basis vectors are called lattice constants. In the Bravais lattice a repetitive unit that can be translated through the vector $\mathbf{T}$, and correctly describe the crystal without overlap or leaving voids, is called a unit cell [14]. Figure 2.1 shows an example of a Bravais lattice and a unit cell.

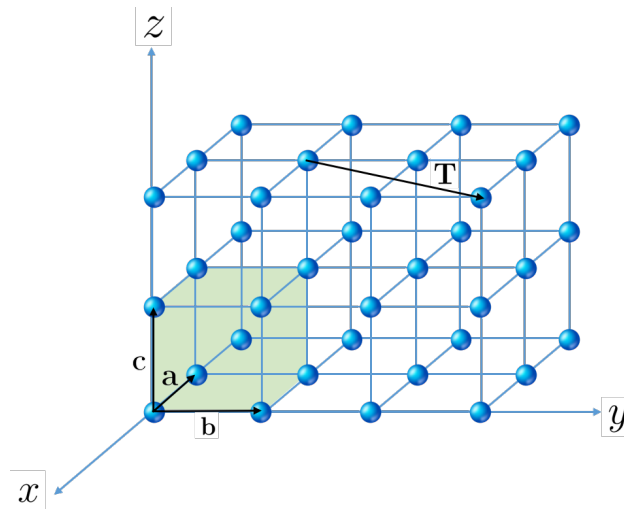


Figure 2.1: An example of a Bravais lattice where the unit cell is shown in green. $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are the basis vectors of the unit cell and $\mathbf{T}$ is the translation vector by which one can move one lattice point to another [1].

An ideal crystal can also be seen as a collection of atom planes where the orientations of these planes are specified by the so called Miller indices or (hkl)-indices. Examples of different crystal planes and their corresponding Miller indices can be seen in Figure 2.2. To find the Miller indices of any crystal plane one can follow three steps:

-Find the intercepts of the plane with the crystallographic axis. In Figure 2.2 the intercepts of the left example are $(1\infty\infty)$.

-Take the reciprocal of these values where the reciprocal of ∞ is defined as 0. For example, the reciprocal of $(1\infty\infty)$ is (100) .

- Reduce the values to the smallest set of integers that have the same ratio to get the (hkl) index of the plane. In the left example of Figure 2.2 this is not necessary.

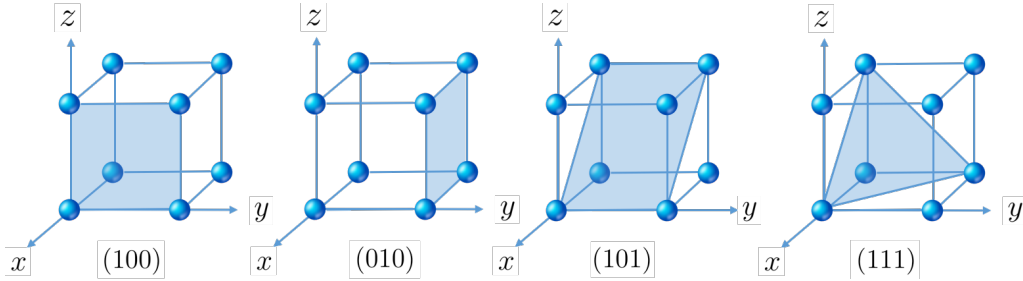


Figure 2.2: Example of Miller indices for different planes of a simple cubic lattice.

One important feature of the crystal lattice is the distance between different (hkl)-planes. This distance is called the interplanar spacing d_{hkl} and Figure 2.3 shows this spacing for different (hkl)-planes in a 2D lattice. The interplanar spacing can be calculated from the following equation [2]:

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}} \quad (2.2)$$

where a , b and c are the length of the basis vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ shown in Figure 2.1. In general, when the Miller indices increase, both the interplanar spacing and the number of atoms per unit area of the plane decreases. [1]

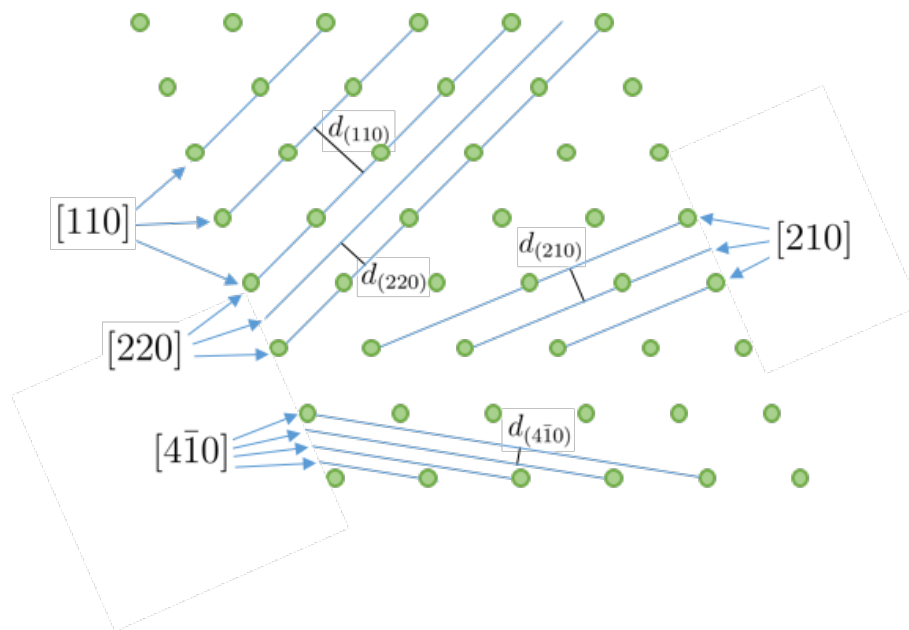


Figure 2.3: Example of crystal planes with corresponding interplanar spacings [1].

2.2 Polymers

Polymers are macromolecules consisting of low molecular weight building blocks called monomers. The process during which polymers are formed is called polymerisation and it involves reactive monomers binding together to form long polymer chains. Depending on the intrinsic nature of the monomers and varying polymerisation parameters, different types of architectures of the polymer chains are possible. Most often the resulting polymers after polymerisation are either linear, branched or crosslinked, see Figure 2.4.

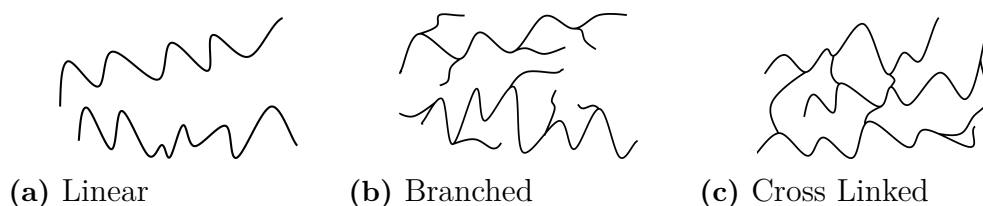


Figure 2.4: Polymer architectures.

2.2.1 Crystalline Phase of Polymers

Polymer materials are often semi-crystalline, which means that they consist of both crystalline and amorphous regions. In the amorphous regions the polymer chains are entangled in a random fashion, while in the crystalline regions the polymer chains are oriented relative to each other.

In the crystalline regions, long enough polymer chains fold back on themselves and form structures called lamellae where the direction of the chain is perpendicular to the lamellae. The structure of a semicrystalline polymer can be seen in Figure 2.5. Individual polymer chains may be involved in more than one lamellae as well as the amorphous regions in between. [15]

In order for crystallisation of a polymer material to take place, the Gibbs free energy, G , must be negative.

$$\Delta G = \Delta H - T\Delta S \quad (2.3)$$

where H is enthalpy, S is entropy and T is temperature. Crystallisation is a process that involves ordering of polymer chains and is consequently associated with a large negative entropy change. Thus, in order for crystallisation to take place there must be a large negative enthalpy change during crystallisation, which means that the interaction between polymer chains must be strong. Linear polymer chains allow for the polymers to pack closely, which increases the interaction between the chains, and thus linear polymers are more prone to form crystals. Since defects, like branching points on the polymer chain, reduce the ability to crystallise, any defect must be excluded from any crystal. In branched polymers, only regions in between branching points will crystallise resulting in reduced lamellae size and crystallinity. A high degree of crystallinity is associated with high stiffness, tensile strength and hardness. [16].

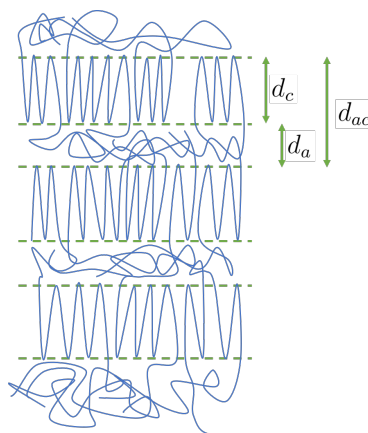


Figure 2.5: The semicrystalline structure of a linear polymer. d_c is the thickness of a crystalline lamella, d_a is the thickness of the amorphous layer and d_{ac} is the thickness of one lamella and one amorphous region [2].

2.2.2 Hierarchic Structure of Polymers

The crystalline lamellae can also arrange themselves into larger scaled ordered structures. Examples of such structures are spherulites, elongated spherulites and shish-kebab structures, as shown in Figure 2.6. The preferred crystal morphology depends on the processing conditions. If the crystallisation process starts from a polymer melt with randomly oriented polymer chains, the melt will form pointlike nucleation, which results in a spherulite morphology. If the polymer chains instead are slightly deformed by the flow, elongated spherulites can form. The elongated spherulites are reported to form from short fiber-like precursors aligned in the flow direction with most of the crystalline lamellae directed perpendicular to the flow [17]. The shish-kebab structure is likely to form when the polymer chains are highly aligned by the flow. In the shish-kebab structure, highly oriented thread-like structures form in the direction of the flow, with the crystalline lamellae growing in the perpendicular direction [18]. Oriented structures such as the shish-kebab structure are reported to be more prone to form when the cooling rate is high [9]. This is generally the case close to the cold walls of the injection mould.

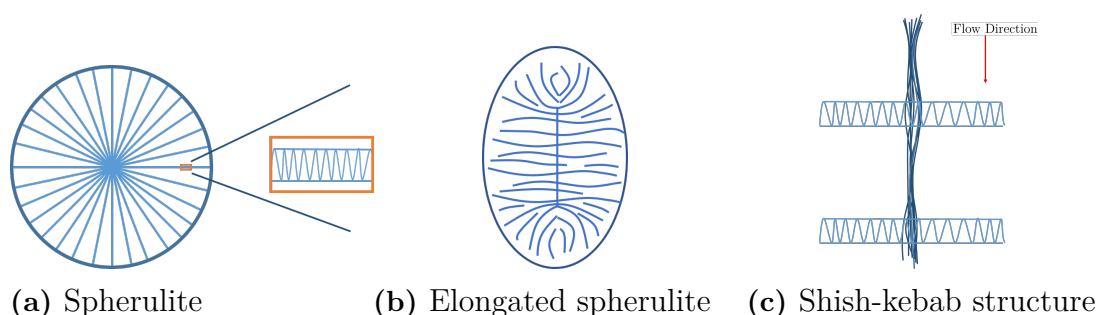


Figure 2.6: Hierarchic structures that semi crystalline polymers may form.

2.2.3 Mechanical Behaviour of Polymers

One of the most important features of a polymer from an industrial point of view is the inherent toughness and resistance to fracture. Thus, studying the mechanical behaviour of polymers is of outermost importance and experimental techniques are well established.

One of the most commonly used techniques to study the mechanical behaviour of polymers is measuring the stress-strain behaviour, since it provides useful information on the modulus, brittleness, and strength of the polymer. During a stress-strain measurement, a tensile force is applied to a specimen and the deformation of the specimen is measured. A typical stress-strain curve of a semicrystalline polymer is shown in Figure 2.7. In region I, the deformation of the polymer is elastic, i.e. the deformation of the polymer is homogeneous and after removal of the applied force the polymer will return to its original shape and size. At high enough deformations, the polymer will reach its elastic limit, and beyond this point the deformation of the polymer will be permanent. This point is called the yield point. Region II starts after the yield point and in this region the polymer has a plastic behaviour. In the plastic region, elongation of the specimen will continue at almost constant stress until the ultimate elongation is eventually reached and the polymer breaks.

The stress-strain behaviour of a polymer is determined by the microstructure of the polymer. Other factors, such as temperature and rate on testing, also effect the stress-strain result and consequently these parameters must be specified in order for a meaningful comparison between tests to be made. If a polymer breaks before the yield point is reached, the polymer is defined as brittle. If the polymer instead elongates in the plastic region the polymer is defined as ductile. [16]

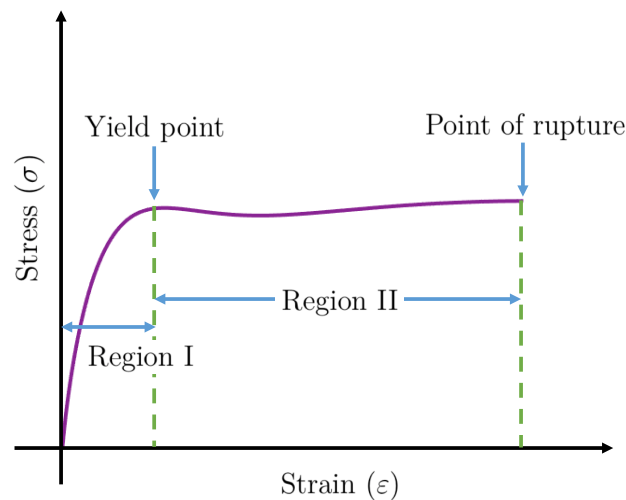


Figure 2.7: A typical stress-strain curve for a semicrystalline polymer.

2.2.4 Polyethylene

A widely used polymer is polyethylene (PE) with the chemical structure shown in Figure 2.8:

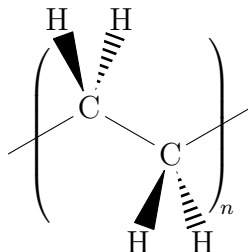
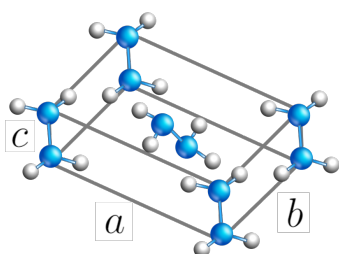


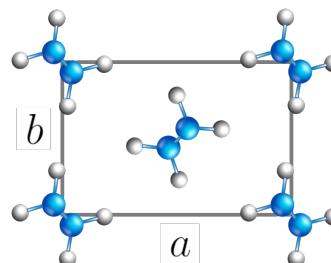
Figure 2.8: The chemical formula of polyethylene.

In PE the polymer chains can order in different configurations. The most common configuration is the orthorhombic, and the unit cell of this configuration can be seen in Figure 2.9. The lattice constants of the unit cell are $a=7.414 \text{ \AA}$, $b=4.942 \text{ \AA}$, $c=2.5473 \text{ \AA}$ at 30°C [19].

Two common types of PE materials are high density polyethylene (HDPE) and low density polyethylene (LDPE). In HDPE the polymer chains have few branching points resulting in higher crystallinity and therefore higher rigidity. LDPE, on the other hand, has several branching points and is thus more flexible.



(a) The unit cell seen from the side.



(b) The unit cell seen from above.

Figure 2.9: The unit cell of orthorhombic polyethylene.

2.3 Injection Moulding of Polymers

Injection moulding is a commonly used process technique for semicrystalline polymers. In an injection moulding process, plastic pellets are fed into the machine and heated until the polymer is soft enough to flow into a mould under pressure.

During injection moulding, the flow of the polymer melt follows a so called fountain flow, as shown in Figure 2.10. The flow pattern will strongly influence the microstructure of the injection moulded material.

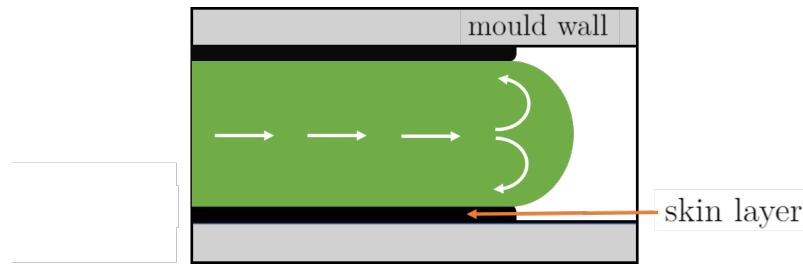


Figure 2.10: The characteristic flow pattern of injection moulding.

In the fountain flow, the injected polymer melt will flow through the central line of the thickness towards the melt front. When approaching the melt front the polymer changes direction from the central line towards the walls of the moulding tools. Because the temperature of the wall is below the transition temperature of the polymer, the polymers that come into contact with the wall will cool rapidly and freeze in place. This creates an isolating skin layer on each wall, which makes it easier for new material to reach the wall. A consequence of fountain flow is that the polymer that was injected first can be found closest to the injection point, as shown in Figure 2.10. [17], [20].

Due to the characteristics of the fountain flow, the velocity of the melt is highest close to the central line and decreases when approaching the wall, as shown in Figure 2.11. Regions with high shear rate, that is regions where the difference in flow velocity is high, will give shear induced orientation of the polymer in the direction of the flow. Close to the central line, both shear rate and temperature gradient will be low, resulting in randomly oriented polymer chains.[3]

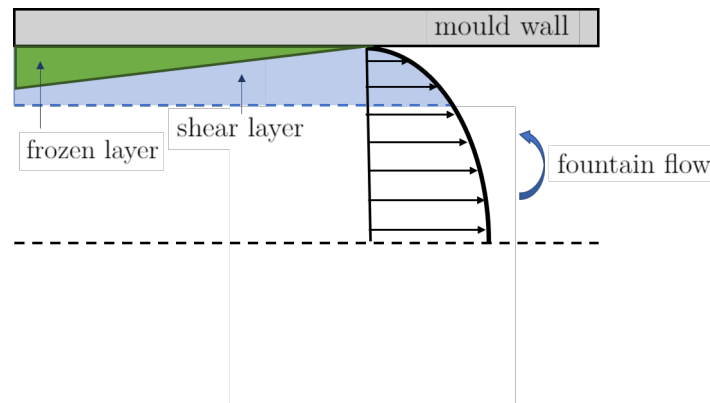


Figure 2.11: The shear rate profile in fountain flow [3].

Due to both temperature gradient and shear rate, the injection moulding of polymer part results in a layered structure through the thickness, as shown in Figure 2.12, where each layer has a different orientation. This will give rise to anisotropic material properties.

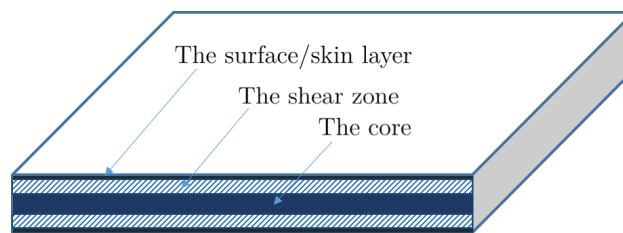


Figure 2.12: Layers in injection moulded polymer plate.

2.4 X-ray Scattering

In order to investigate the microstructure of polymers, X-ray scattering can be used. X-ray scattering methods are accurate and non-destructive and require minimum sample preparation [21].

The working principle of X-ray scattering techniques is that a monochromatic focused X-ray beam interacts with the electrons in the sample and the intensity of the scattered X-rays is recorded by a detector, as illustrated in Figure 2.13. The diffraction pattern detected is the Fourier transform of the electron density distribution within the unit cell of the crystal [1]. The scattering behaviour of X-rays can be explained by Bragg's law:

$$n\lambda = 2d\sin(\theta) \quad (2.4)$$

where n is a positive integer, λ is the wavelength of the X-rays, d is the distance between the repeating structure and θ is the scattering angle. When Bragg's law is fulfilled, there will be constructive interference that gives a diffraction peak in the scattering pattern.

Bragg's law can be derived from Figure 2.14. The lower X-ray beam travels an extra distance of $2AB$. In order for constructive interference to take place, X-rays scattered on parallel atom planes must have the same phase after the scattering event. This is accomplished when the path difference between the X-rays is an integer times the wavelength λ , which mathematically can be described as $2|AB| = n\lambda$. By applying trigonometry, the distances $|AB|$ can be expressed as $|AB| = d\sin(\theta)$. By combining these expressions, Bragg's law is obtained: $n\lambda = 2d\sin\theta$

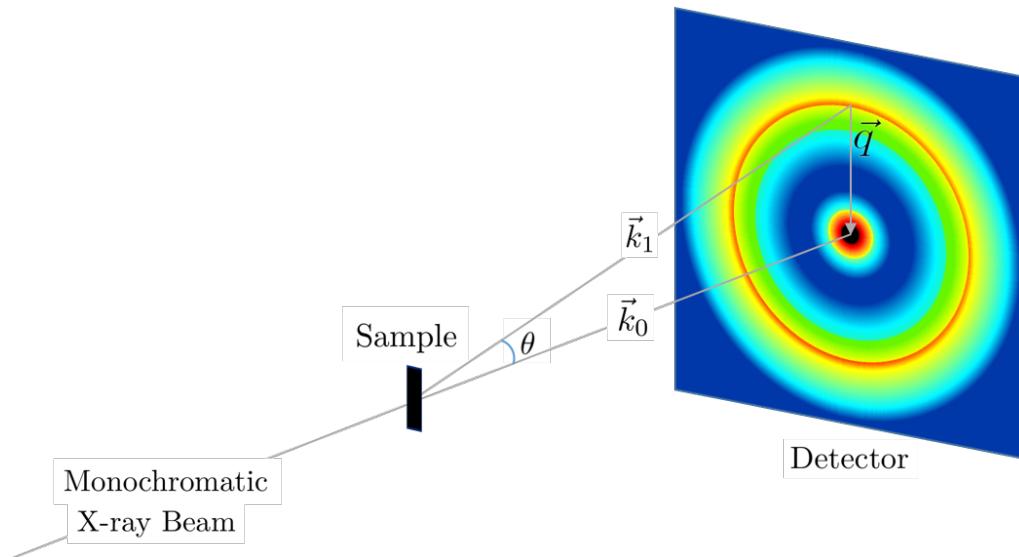


Figure 2.13: The experimental setup of SAXS/WAXS.

According to Bragg's law, the diffraction peaks directly correspond to a repeating unit in the material and by studying the scattering pattern information about the microstructure can be obtained [1].

When analysing a scattering pattern, it is convenient to define a wave vector $\vec{q}$ as

$$\vec{q} = \vec{k}_0 - \vec{k}_1 \quad (2.5)$$

where $\vec{k}_0$ is the wave vector of the incoming X-rays and $\vec{k}_1$ is the wave vector of the scattered X-rays under the angle θ , as shown in Figure 2.13. In the case of elastic scattering, the energy and thus the wavelength must be equal for both incoming and scattered X-ray, which gives that $|\vec{k}_0| = |\vec{k}_1| = 2\pi/\lambda$ [2]. The wave vector $\vec{q}$ can then be described as

$$|\vec{q}| = q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (2.6)$$

By combining Equation 2.4 and 2.6 a simple relationship between the repeating distance d and q can be established by

$$d = \frac{2\pi}{q} \quad (2.7)$$

In X-ray scattering, large structural features in the system correspond to small scattering angles and small q -values. Hence, Small Angle X-ray scattering (SAXS) is used to investigate relatively large scattering structures in the range of a few nanometers to hundreds of nanometers. In semi-crystalline polymers, these are typical dimensions for lamellae spacing, the distance between different crystalline regions, see Figure 2.5. Wide Angle X-ray Scattering (WAXS), also called X-ray diffraction (XRD), can detect features at sub-nanometer scale and is used to determine the spacing between different atom planes as in Figure 2.3. Furthermore, WAXS can provide information about the averaged distance between atoms in the amorphous regions. The detectable scattering angles can be varied by changing the distance between the sample and the detector. [22]

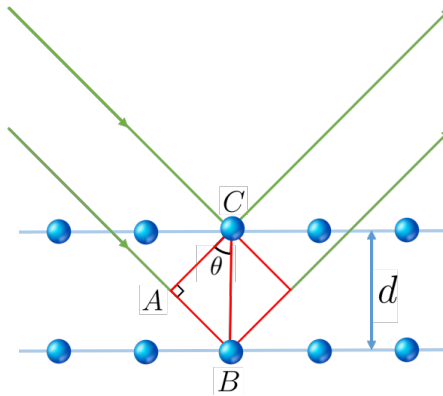


Figure 2.14: X-rays scattering on two neighbouring atom planes.

2.4.1 X-ray Scattering of Polyethylene

According to Bragg's law, an intensity maximum in a scattering pattern corresponds to the distance between a repeating structure in the sample. PE has structural characteristics on several length-scales and thus, when performing SAXS and WAXS on PE several different scattering peaks can be measured.

At small length-scales, as measured with WAXS, the repeating distances are the distances between atom planes d_{hkl} . In the crystalline regions of PE the material has both short- and long range order and the positions of the atoms are well defined. Hence, these distances will give rise to sharp peaks. In the amorphous region the material lacks long range order. Nevertheless, a short range order is still present due to chemical bonds between atoms [2]. Since the inter-atomic distances vary more in the amorphous region than in the crystalline, the amorphous peak are broader and less well-defined.

Being semicrystalline, polyethylene also shows repeating structures on larger length-scales since it consists of alternating crystalline and amorphous regions. The crystalline lamellae have a characteristic thickness d_c and the amorphous layers show an average thickness d_a . These two distances can be added up to a repeating distance that includes one crystalline and one amorphous region d_{ac} and can be measured with SAXS. The repeating units of a semicrystalline polymer can be seen in Figure 2.5.

2.5 Scanning Electron Microscopy

The resolving power of any type of microscopy is limited by the wavelength of the particles used to illuminate the sample. Since the wavelength of electrons are shorter compared to the wavelength of photons of visible light, electron microscopes can produce images with a higher magnification compared to optical microscopes [23]. Thus, Scanning Electron Microscopy (SEM) is a commonly used technique for analysing the microstructure of a sample.

The working principle of SEM is that an electron beam is scanned over the sample, upon the electrons interact with the sample producing various signals [3]. One of the most widely used signals is the signal from secondary electrons. When the incoming electron beam strikes over the sample it will ionise some of the atoms, causing secondary electrons to be emitted. Secondary electrons have very low energy, typically around 3-5 eV, and can thus only escape from the sample if emitted in a region within a few nanometers from the sample surface. Thereby, secondary electrons give topographical information from the sample with high resolution.

3

Experimental Methods

3.1 Material

The materials used for preparing the injection moulded test plates was a medium viscosity LDPE and a low viscosity LDPE, both with a density of 923 kg/m^3 . The Melf Flow Index (MFI) for the medium viscosity LDPE is 22 g/10 min and for the low viscosity LDPE 55 g/10 min when measured at 190° at a load of 2.16 kg .

When preparing the pigmented samples, pigment was added to the polymer in the same ratio as the commercially available equivalents at Tetra Pak[®]. Thus, the pigmented medium viscosity LDPE was prepared with 2.5% pigment while the low viscosity LDPE was prepared with 5% pigment.

3.2 Sample Preparation

Three different types of samples were used:

- Samples from test plate, undeformed.
- Samples from test plate, deformed by tensile testing
- Samples from commercially available products

The test plates were prepared by using the injection moulding machine Arburg All-rounder 470 S at Tetra Pak[®]. The dimensions of the test plates can be seen in Figure 3.1. MD is an abbreviation of machine direction and corresponds to direction of the flow, while CD is an abbreviation for cross directions corresponds to the direction perpendicular to the flow.

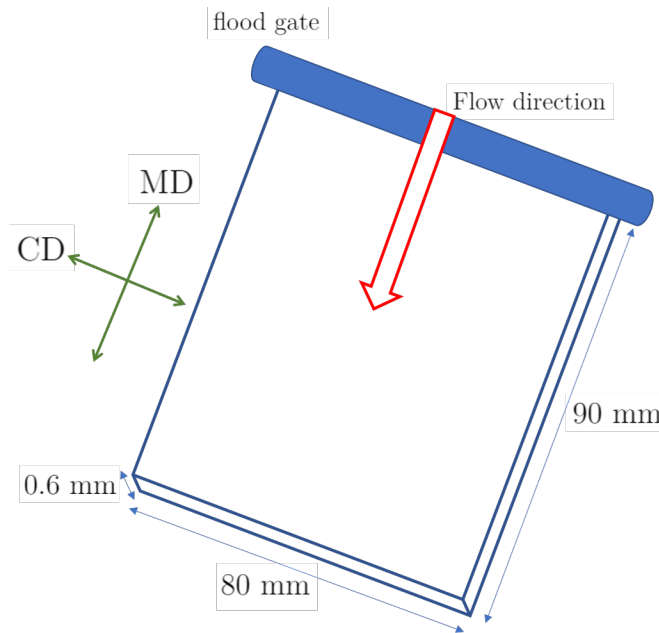


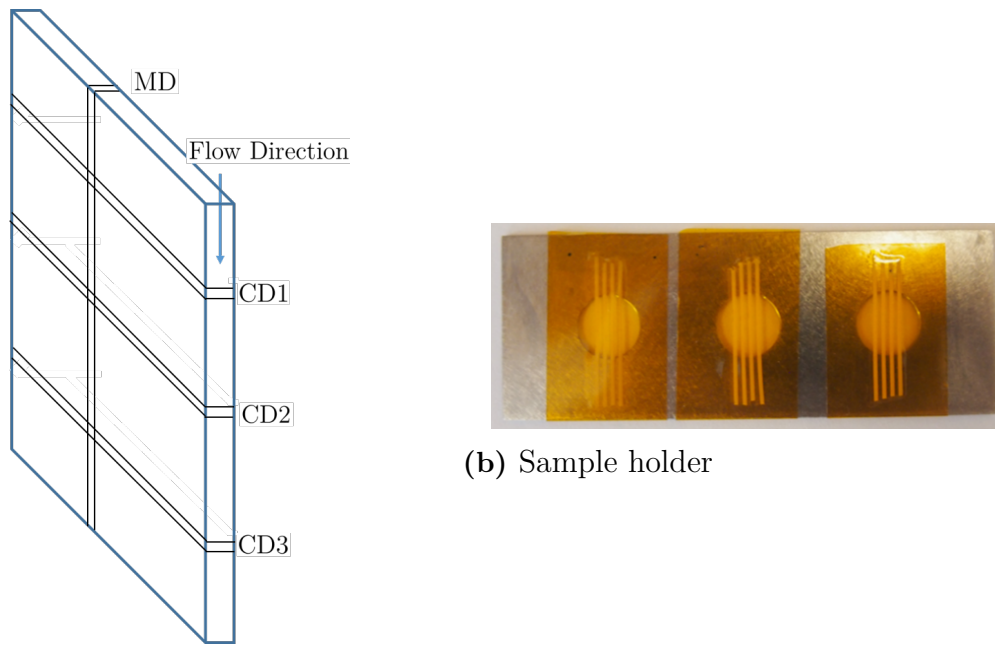
Figure 3.1: Dimensions of the injection moulded test plate.

The undeformed samples from the test plate was prepared by cutting out slices of thickness $50\ \mu\text{m}$ in positions CD1, CD2, CD3 and MD by using an microtome of model Leica RM2255, as shown in Figure 3.2a. The samples were then put on Kapton tape and taped to a sample holder, as shown in Figure 3.2b. The sample holder consisted of a metal plate with three circular holes where X-rays could radiate through the samples. In each hole, eight test plates were put next to each other, where pigmented and unpigmented samples were altered. This was done in order easier distinguish between samples when analysing the scanning SAXS/WAXS data. The Kapton tape used was a polyimide film with silicon adhesive [24], which gives

low background values for SAXS and WAXS measurements.

The samples used for tensile testing were prepared by punching out specimens shaped as dogbones in position CD1, CD2, CD3 and MD, as shown in figure 3.3. The dogbone samples were deformed until fracture during stress-strain tensile testing and the deformed areas were measured with scanning SAXS and WAXS.

For samples from commercially available products interesting regions were cut out by using a scalpel.



(a) Samples prepared from test plate

Figure 3.2: Preparation of samples from test plate.

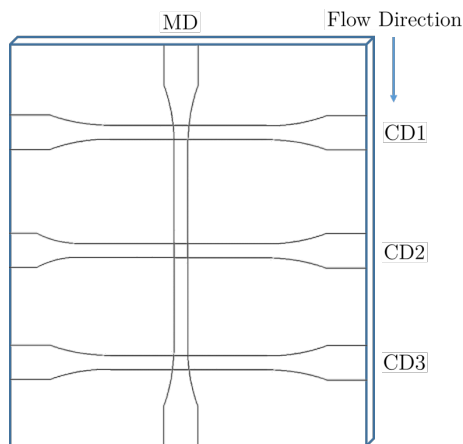


Figure 3.3: Preparation of dogbone-shaped samples for tensile testing.

Samples were prepared for scanning SAXS and WAXS measurements in top view and side view, as shown in Figure 3.4. The top view mode was used to investigate different areas of the samples. In the top view mode, an average electron density through the thickness of the test plate is measured. This experimental setup was used at both laboratory source at CMAL and Synchrotron source at Swiss Light Source (SLS). The side view mode was used to examine the layered structure of the thickness in the injected moulded samples. Since the test plates were only 0.6 mm thick, good spatial resolution was needed. Thus, the side view experiments were performed at SLS.

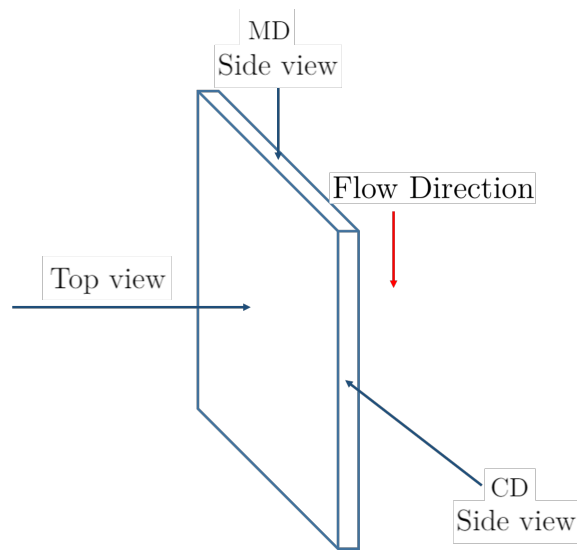


Figure 3.4: Side view and top view.

3.3 X-ray Diffraction Experimental Setup

X-ray diffraction experiments were performed at two different experimental stations.

- Laboratory X-ray source SAXSLAB Mat:Nordic at Chalmers Materials Analysis Laboratory (CMAL).
- Synchrotron X-ray source cSAXS beamline X12SA at Swiss light source (SLS) at the Paul Scherrer Institute (PSI) in Switzerland.

The working principle of SAXS and WAXS is the same at both experimental stations: X-rays interact with the electrons in the sample and the scattering behaviour is detected and analysed. The main difference lies in the brilliance of the X-rays produced. The brilliance of an X-ray beam takes into account the flux, focus, monochromaticity, and source size of the X-ray beam. [1]

At the synchrotron source, the X-ray photons are produced by accelerating electrons to near light speed and then forcing them to change direction by using magnetic fields. This results in an X-ray beam with a very high brilliance. All experiments at the cSAXS beamline X12SA, SLS, were carried out by using scanning SAXS/WAXS, i.e. a sample was scanned through a focused X-ray beam where a scattering pattern was collected for each position of the scan. This opened up the opportunity to investigate how different nanoscale material properties, such as the degree of orientation, changed throughout extended areas of the sample. The stepsize of the scan was varied between 20-40 μm .

At the laboratory based source at CMAL, the X-rays are produced by a Rigaku 003 X-ray Microfocus Cu-Radiation source [25]. In this system, electrons are accelerated and collided into a copper target, which causes X-ray photons to be emitted. Compared to a synchrotron, laboratory based X-ray beams have limited flux and thus much longer exposure times are needed in order to get high spatial resolution with sufficient statistical quality [26]. Thus, scanning SAXS was not possible at the laboratory source and instead point measurements were taken at different positions of the sample. Experimental parameters for both the synchrotron and laboratory based sources are shown in Table 3.1.

In conclusion, the strength of a synchrotron lies in the brilliance of the X-ray beam produced, while the strength of a laboratory source instead lies in the accessibility of the instrument. Therefore, the laboratory source was mostly used for preliminary studies, such as finding interesting samples and sample regions, for subsequent measurements at the synchrotron source.

Table 3.1: The experimental parameters for the SAXS and WAXS configurations for the measurements performed at CMAL and PSI.

X-ray Source	Measurement type	beam size	Exposure time	q -range
Synchrotron based source	SAXS	100 nm-100 μm^*	0.1-0.2 s ^{**}	0.006-0.56 $\text{\AA}$
	WAXS	100 nm-100 μm^*	0.1-0.2 s ^{**}	0.65-2.77 $\text{\AA}$
Laboratory based source	SAXS	0.1-0.3 mm	5-60 min	0.007-0.25 $\text{\AA}$
	WAXS	0.9 mm	3 min	0.07-2.7 $\text{\AA}$

3.4 Processing and Interpretation of Scattering Data

The raw data obtained from a SAXS or a WAXS measurement is a 2D scattering pattern. However, it can be hard to directly interpret all the information that lies within the scattering pattern and thus data reduction is most often needed.

From the 2D scattering data, the data was reduced to one dimension by using radial integration. The reduced data is represented as a plot with the scattering intensity on the y-axis and the q -value on the x-axis.

The radial integration was done in two different ways:

- Integrating the intensity over all angles
- Integrating the intensity for a smaller range of angles

By doing the second option and then compare different angle segments, the anisotropy of the sample was evaluated. Figure 3.5 shows the radial integration of two different angular segments 1 and 2.

In addition to the radial integration, azimuthal intensity distribution plots were also constructed. This was done by plotting the scattering intensity as a function of the azimuthal angle for a specific q -value, as shown in Figure 3.6. Three important features in the azimuthal intensity distribution plot are the symmetric intensity a_0 , which correspond to the mean scattering intensity, and the asymmetric intensity a_1 , which correspond to the maximum scattering intensity. The degree of orientation depends on how asymmetric the scattering pattern is and is defined as [27]:

$$\text{Degree of orientation} = \frac{a_1}{a_0} \quad (3.1)$$

*The beam size of a synchrotron based source is highly dependent on the beamline used

**The exposure time could be reduced since the signal had very high statistical quality

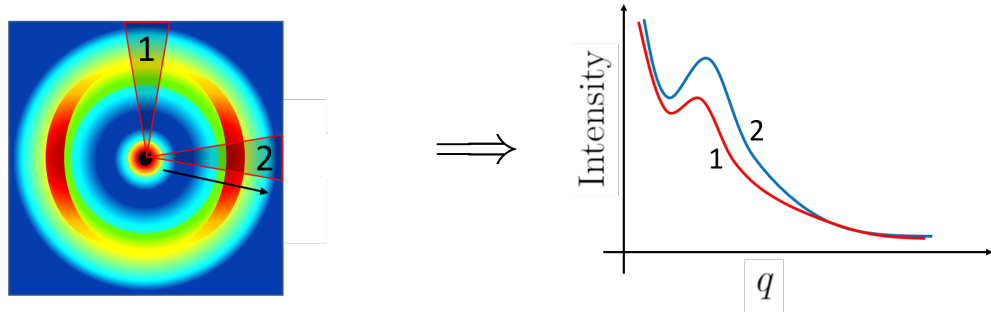


Figure 3.5: X-ray scattering pattern and radially integrated data averaged for sectors 1 and 2 as indicated in the scattering pattern.

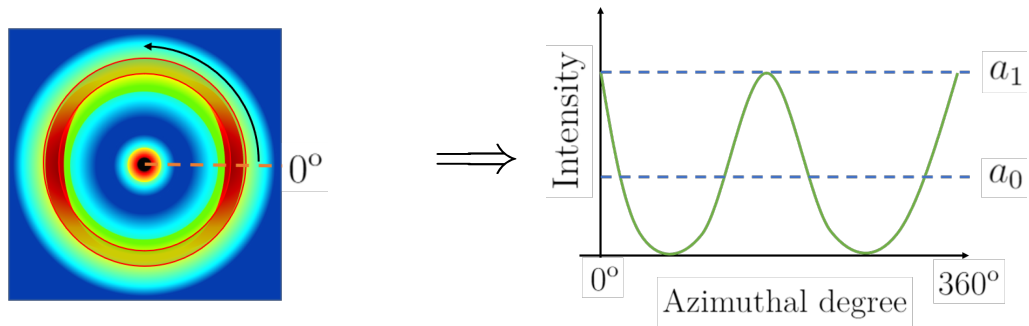


Figure 3.6: X-ray scattering pattern and azimuthal intensity distribution plot averaged for the q -region indicated in the scattering pattern.

For the scanning SAXS measurements, the data reduction was carried out by using the “cSAXS scanning SAXS package” developed by the CXS group at PSI. The scanning SAXS package analyse each scattering pattern and the result is displayed as images showing how one of the following scattering properties changes in the selected area:

- Symmetric amplitude, where a bright areas in the image correspond to high average scattering intensity
- Assymmetric amplitude and orientation, where the colour correspond to the direction with highest scattering intensity, and the intensity of the colour correspond to the difference between the maximum and the average scattering intensity.
- Degree of orientation, where bright areas in the image correspond to a highly ordered scattering patterns and dark areas correspond to scattering patterns with no preferred scattering direction.

4

Results and Discussion

4.1 Quantifying the Diffraction Signal of PE

An example of a radial integrated diffraction signal taken from the bulk layer of medium viscosity LDPE in side view is shown in Figure 4.1. In the SAXS data a broad peak [a] is clearly visible. This peak is reported to correspond to the repeating distance d_{ac} that includes one amorphous and one crystalline layer, as illustrated in Figure 2.5 [2]. The large peak width implies that there is a large variety of d_{ac} present in the sample.

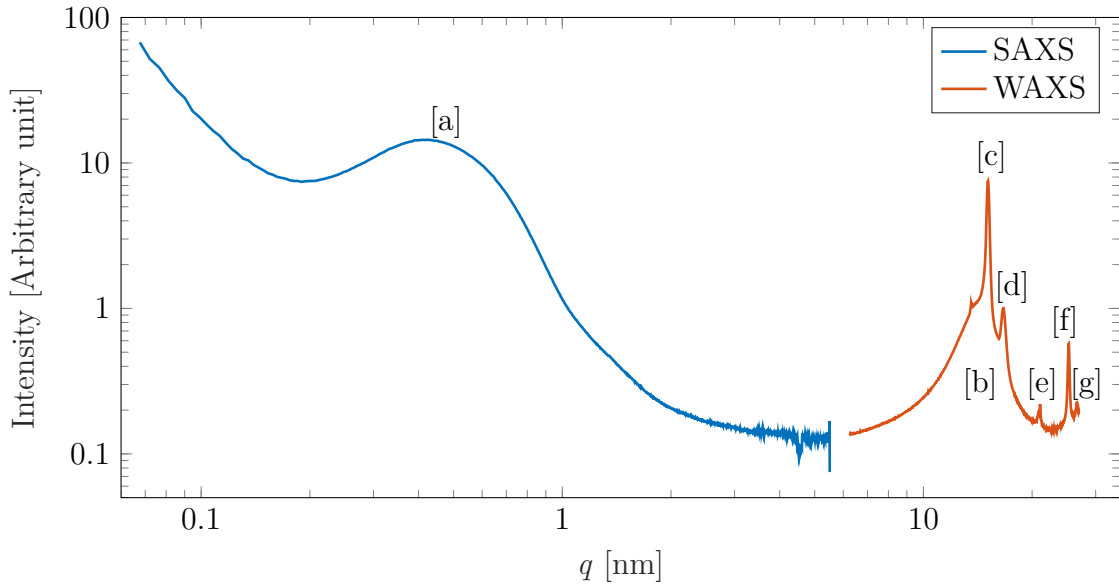


Figure 4.1: Diffraction pattern of the bulk layer of medium viscosity LDPE, taken in side view. The SAXS signal is shown in blue and the WAXS signal is shown in red.

In the WAXS regime, the diffraction peaks correspond to inter-molecular distances. In the crystalline regions, these distances can be described as the spacing between different atom planes, as shown in figure 2.3. Since the molecules in a crystal have well defined positions, this will give rise to diffraction peaks with narrow peak width. In Figure 4.1, the sharp peaks [c-g] is a result of diffraction in the crystalline region. The broad peak [b], instead correspond to the inter-molecular distances in the amorphous region, where the peak position is defined by the average distance between the molecules in this region.

From the diffraction peaks, the corresponding repeating distance d was calculated by equation 2.7. For the crystalline WAXS peaks, the d -values was compared to theoretical d -values calculated from equation 2.2, where the lattice constants from a study carried out by *Swan* was used as input [19] ($a = 7.414 \text{ \AA}$, $b = 4.942 \text{ \AA}$). By comparing the theoretical and observed WAXS peaks, the corresponding crystal plane could be determined. The result is summarised in Table 4.1.

Table 4.1: Characterisation of the diffraction peaks of PE. The table summarises the q -value, the calculated d -value, the crystal plane and the theoretical d -value for each peak.

Peak	$q \text{ [nm}^{-1}\text{]}$	$d \text{ [nm]}$	Crystal plane (hkl)	Theoretical $d \text{ [nm]}$
[a]	0.424	14.82	-	-
[b]	~ 14.8	~ 0.42	-	-
[c]	15.10	0.416	(110)	0.4112
[d]	16.64	0.378	(200)	0.3707
[e]	21.04	0.299	(210)	0.2965
[f]	25.27	0.249	(020)	0.2471
[g]	26.62	0.236	(120)	0.2344

4.2 Preliminary Studies at CMAL

Comparison Between Different Areas of Test Plates

Aiming to investigate how the diffraction signal varied at different positions of the test plates, four different points were measured in top view for medium viscosity LDPE test plate, as shown in Figure 4.2a. The radial integrated SAXS data is shown in Figure 4.2b

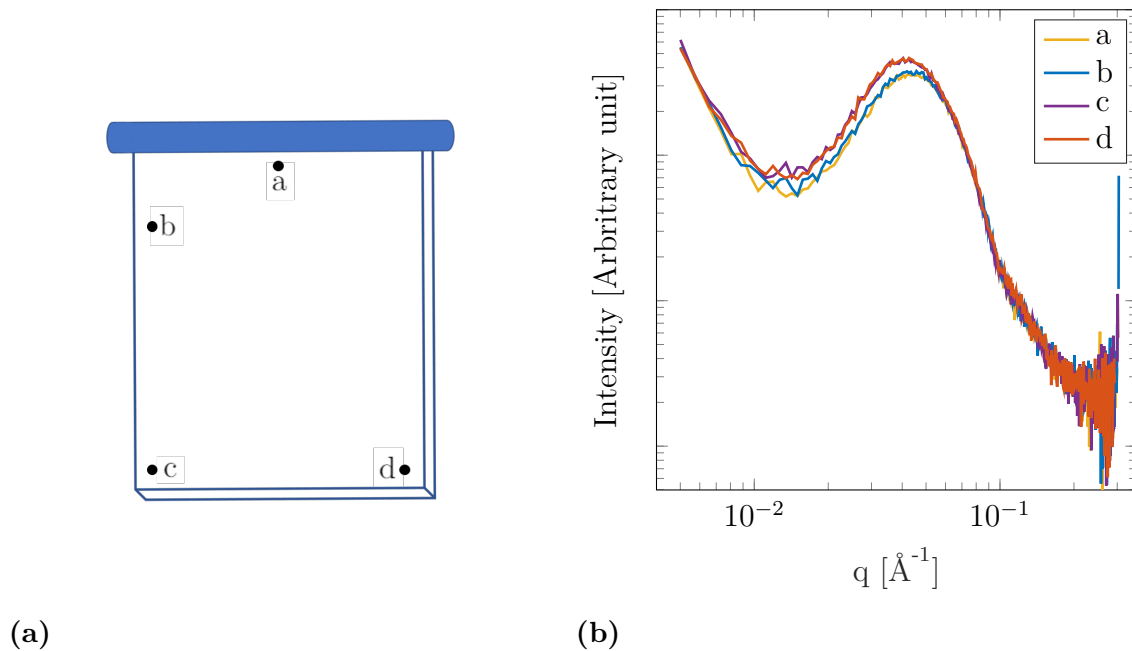


Figure 4.2: Radially integrated SAXS data for four different positions a, b, c and, d of a medium viscosity LDPE test plate.

Figure 4.2b shows that measurements in the bottom of the plate give a stronger SAXS peak compared to corresponding measurements from the top of the test plate. However, no difference in SAXS signal could be seen between samples with the same vertical, but different horizontal positions. Based on these measurements, it was decided to prepare samples with different vertical positions for the synchrotron (CD1, CD2 and CD3) all taken from the same horizontal position (center line of the plate).

Preliminary Studies of Dogbone-Shaped Samples Deformed by Tensile Testing

Prior to the synchrotron measurements at the cSAXS beamline X12SA (SLS), preliminary measurements of the dogbone-shaped samples were performed at CMAL, aiming to investigate if the scattering patterns were changed upon deformation. In addition, the WAXS data from the study was later used as a complement to the scanning WAXS data from cSAXS beamline X12SA (SLS). The reason for this was that the WAXS detector at CMAL could detect in all angles, while the WAXS detector at SLS only detected in a small angle segment. Worth noticing is that the measurements at CMAL were performed on pigmented samples.

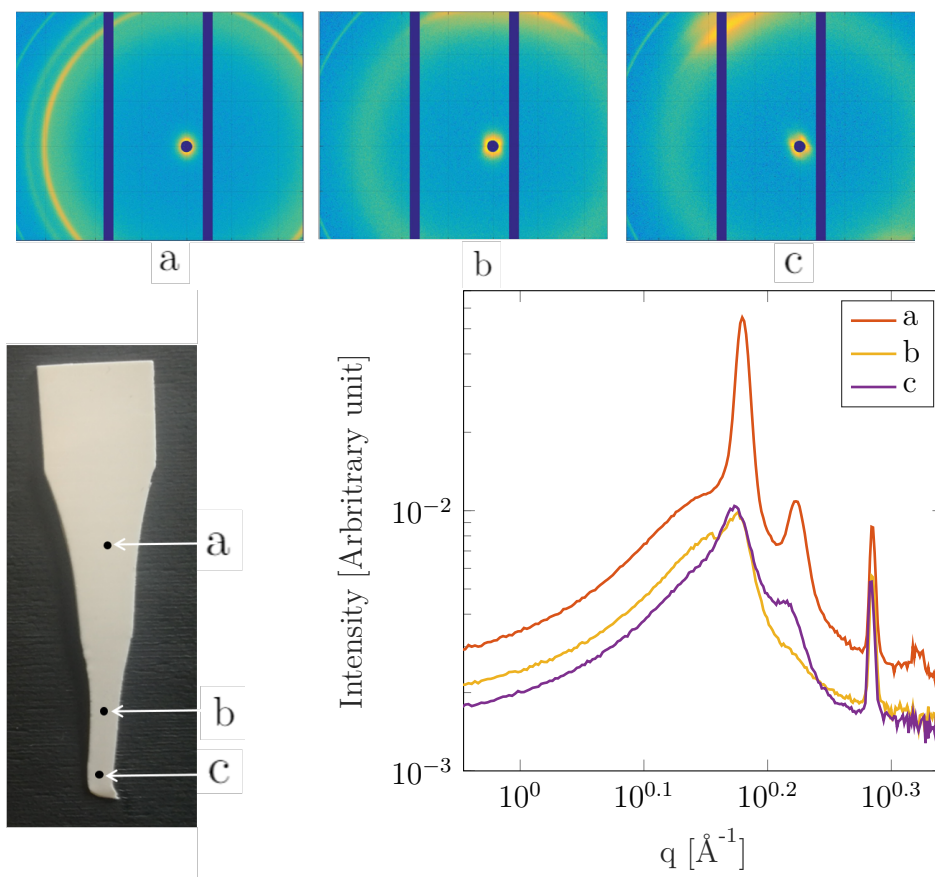


Figure 4.3: WAXS result for a sample deformed in CD. The position of the three points measured is shown together with the raw- and radially integrated data from each point.

Figure 4.3 shows the WAXS raw data and the integrated data averaged over all angles for three different points of a sample deformed in CD. Position (a) was taken at a region before the necking region and was assumed to be relatively undeformed. When entering the deformed part of the sample (b-c) the WAXS scattering pattern becomes highly anisotropic. This indicates an increase of orientation in the sample. Unfortunately, the main intensity of the anisotropic crystalline peak in the deformed region (b-c) is located slightly outside the detectable region of the WAXS detector. Thus, when performing the radial integration of scattering pattern b and

c, the intensity will be lower compared to peak a. Even though the detector could not detect the complete scattering pattern in WAXS, the scattering data still shows that there is a drastic change in scattering behaviour between the undeformed and necked region. The dark blue, vertical lines in the scattering patterns are due to space between different modules of the WAXS detector which does not contain single photon counting pixels.

Figure 4.4 shows the corresponding WAXS measurement for a sample deformed in MD. In the MD samples, no necking region could be identified. Correspondingly, only a very small difference in scattering behaviour can be seen between the different points in the raw and radially integrated data. However, from these measurements it could not be concluded whether there were no change in orientation of the material upon deformation, or if there were local variances that were missed due to the few points measured and the averaging properties of the large beam size of the X-ray beam.

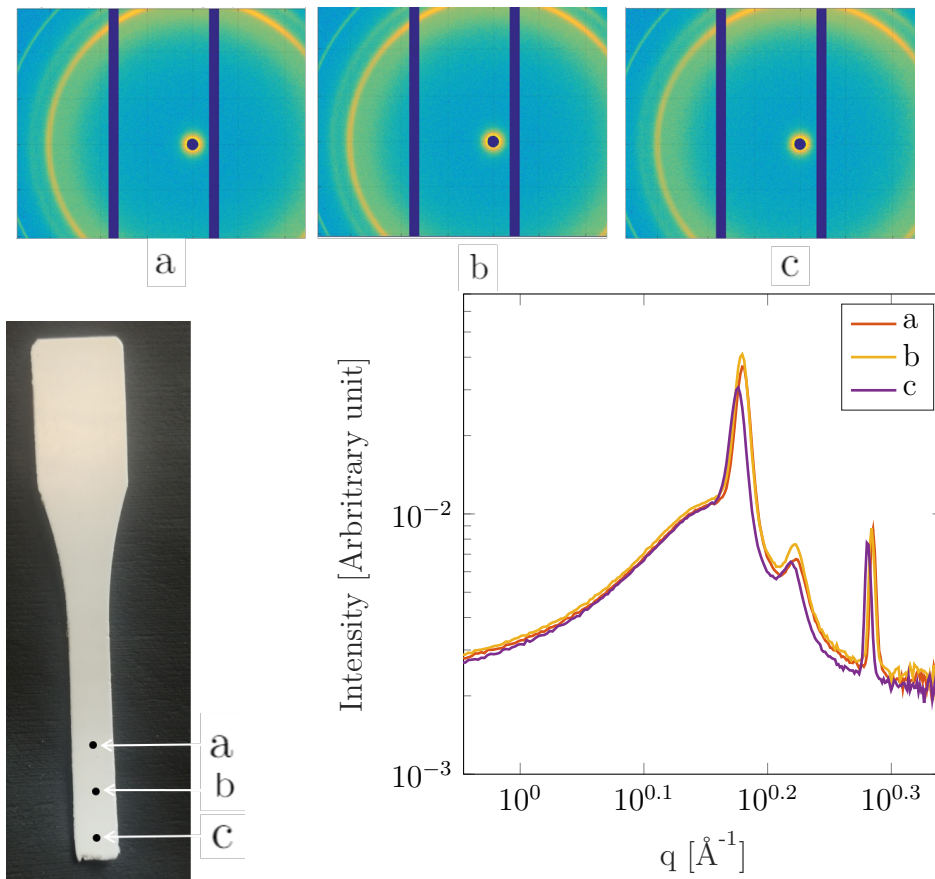


Figure 4.4: WAXS result for a sample deformed in MD. The position of the three points measured is shown together with the raw- and radially integrated data from each point.

From the measurements made at CMAL, it could be concluded that both samples deformed in MD and CD were of interest for the scanning SAXS/WAXS measurements at the cSAXS beamline X12SA (SLS).

4.3 Scanning SAXS and WAXS of Test Plates

The test plates were constructed with a much simpler geometry and flow pattern compared to the commercial available products. Thus, scanning SAXS/WAXS measurements of the test plates indicates more general material properties of injection moulded polyethylene.

Comparing Scanning SAXS to Optical Microscopy

Prior to this thesis, Light Optical Microscopy (LOM) images were taken under polarised light at Tetra Pak[®] aiming to investigate the microstructure of injection moulded polymers through the thickness. An example of such an image of medium viscosity LDPE taken in side view, is shown in Figure 4.5a. A layered structure in the thickness is clearly visible, where 1 is assumed to be the skin layer, 2 the shear layer and 3 the bulk layer. The different layers are visible in LOM since the molecules have different molecular ordering in the different layers [28].

Compared to LOM, SAXS and WAXS have several advantages when investigating the anisotropic material properties of semicrystalline polymers. First of all, LOM is limited to transparent samples, where SAXS and WAXS can be used to measure both transparent and opaque samples. This is of great importance to Tetra Pak[®], since they most often use pigments in their commercially available products. Second of all, LOM can only be used to visualise the layered structure of injection moulded samples, while scanning SAXS and WAXS can be used to also give information about the underlying nanostructure.

A degree of orientation plot from the scanning SAXS measurement was made for both an unpigmented sample, as shown in Figure 4.5b, and a pigmented sample as shown in Figure 4.5c. From the LOM- and the scanning SAXS images of the unpigmented sample it can be seen that both experimental techniques give similar results: three clearly visible layers with approximately the same thicknesses. However, in the LOM image several additional fine lines can be seen, which are not present in the scanning SAXS image. This could either be due to artefacts created when cutting the sample with the microtome, or due to some inherent structures of the polymer that are too small to be resolved in the scanning SAXS measurement where the stepsize was 40 μm .

When comparing the scanning SAXS images of the unpigmented and the pigmented sample, it can be seen that the thickness of the skin- shear and bulk layers are slightly different in the two samples. In addition, the shear- and the bulk layer is less oriented in the pigmented sample compared to the unpigmented sample. Thus, from the scanning SAXS images it can be concluded that the pigment will effect the microstructure formed. In order to measure the impact of the pigment, scanning SAXS is needed since LOM is limited to transparent samples.

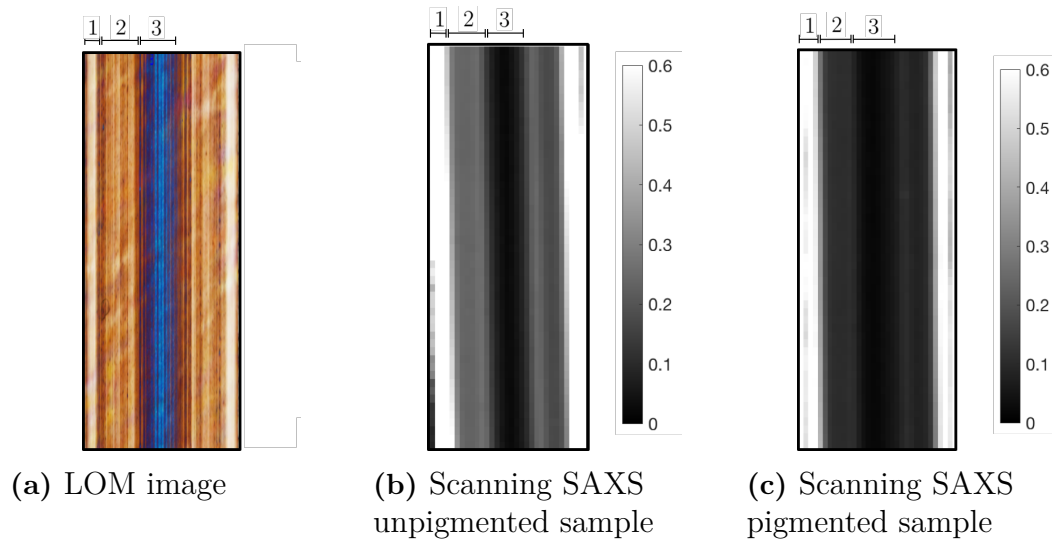


Figure 4.5: Visualisation of the layered structure of medium viscosity LDPE by using (a) polarised light optical microscopy for sample a without pigment, (b) scanning SAXS symmetric amplitude for a sample without pigment and c) scanning SAXS symmetric amplitude for a sample with pigment

Comparing CD to MD

Comparing the scanning SAXS images in MD and CD2 is a way to evaluate the anisotropic microstructure of the sample, since MD and CD2 correspond to the same position of the sample but viewed from different directions. Figure 4.6 shows the comparison of the symmetric amplitude, raw data, degree of orientation and asymmetric amplitude between CD2 and MD.

Figure 4.6 shows that the skin layer consists of a highly ordered structure for both CD2 and MD. This can be seen both in the degree of orientation plots and in the scattering patterns 1 and 4. For CD2, the scattering patterns consisted of a narrow horizontal streak, which is characteristic for fibre-like structures. Since the scattering patterns always have a 90° phase shift from the orientation of the material, this corresponds to a structure oriented in the flow direction. In the MD direction, the scattering pattern is characterised by a similar, weaker horizontal streak and a two point pattern in the vertical direction. The two point pattern is characteristic for stretched out lamellae oriented perpendicular to the flow direction. These scattering patterns indicates a shish kebab structure, as shown in Figure 2.6c, and they are in good agreement with other SAXS studies of shish kebab structures of polymer materials [9, 5, 12].

In the shear and bulk layer of the material, the scattering patterns are less ordered, as shown in scattering pattern 2-3 and 5-6. A circular scattering pattern with no preferred orientation is typical for spherulite microstructure, see Figure 2.6a. However, in the shear layer in MD, the asymmetric amplitude plot shows that the scattering patterns are elongated in the horizontal direction. Such scattering patterns could arise if the microstructure consisted of elongated spherulites with the

long axis oriented in the flow direction and most lamellae directed perpendicular to the flow, as shown in Figure 2.6b.

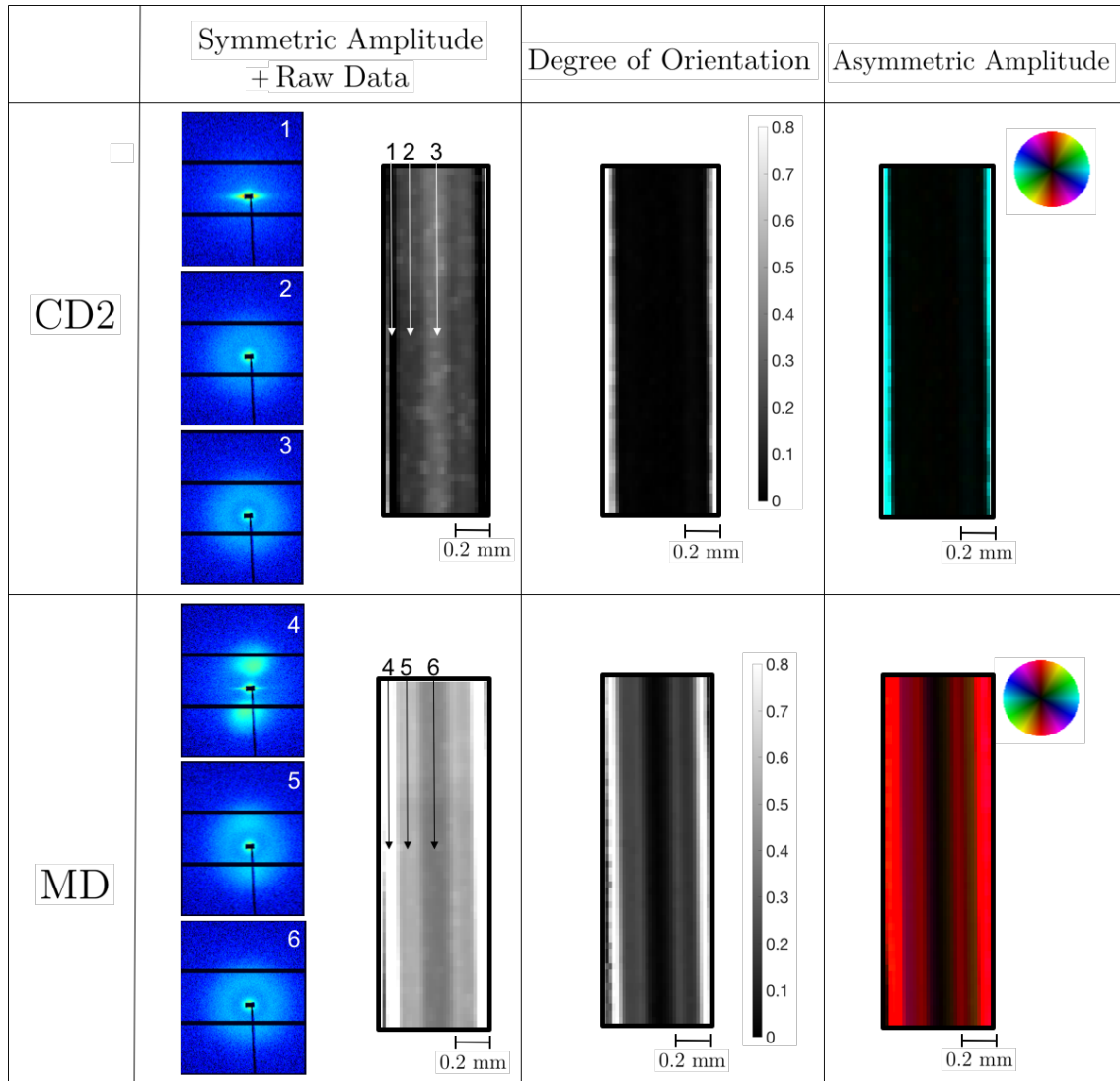


Figure 4.6: Symmetric amplitude with scattering patterns for some selected areas, degree of orientation and asymmetric amplitude for medium viscosity LDPE at position CD2 and MD.

If the elongated spherulites would be completely aligned with the flow, seen from CD they would appear isotropic. This would explain why there is almost no difference between the bulk and the shear layer in the degree of orientation and the asymmetric amplitude plot in CD2. In the bulk layer, the scattering properties are almost identical in MD and CD2, which is consistent with isotropic spherulites.

In conclusion, the characteristic scattering patterns in the skin layer indicates that this layer consists of shish-kebab structures where the fiber-like shish are elongated in the flow direction and the lamellae are elongated perpendicular to the flow. The proposed microstructure of the shear layer is elongated spherulites while the isotropic

scattering of the bulk layer suggests a spherulite microstructure. The proposed microstructure can be seen in Figure 4.7

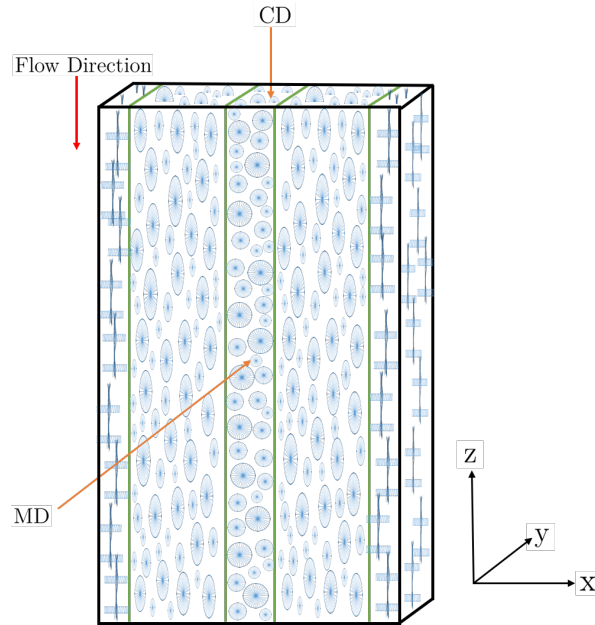


Figure 4.7: The proposed microstructure of injection moulded polyethylene.

Comparing Different Positions of the Test Plate

Aiming to evaluate not only the anisotropy through the thickness but also the anisotropy at different positions of the test plates, symmetric amplitude plots were constructed from both scanning SAXS and WAXS at the positions CD1, CD2 and CD3, as shown in Figure 4.8. The symmetric amplitude for WAXS was plotted for two different q regions, corresponding to the q regions of the two first WAXS peaks shown in Figure 4.1. These peaks are the (110)- and the (200)-peak. Since the SAXS data only contained one peak, only one symmetric intensity plot for scanning SAXS was constructed.

Figure 4.8 shows that a layered structure is visible for both scanning SAXS and scanning WAXS. It also illustrates that the layered structure changes noticeably between CD1, CD2 and CD3. For example, in the shear layer the (200) WAXS peak is much more present in CD3 compared to CD1. The difference of scattering behaviour between CD1, CD2 and CD3 is believed to be a consequence of the different flow patterns at the different positions. Other parameters, such as difference in temperature gradient and pressure could also explain the difference in microstructure between the positions.

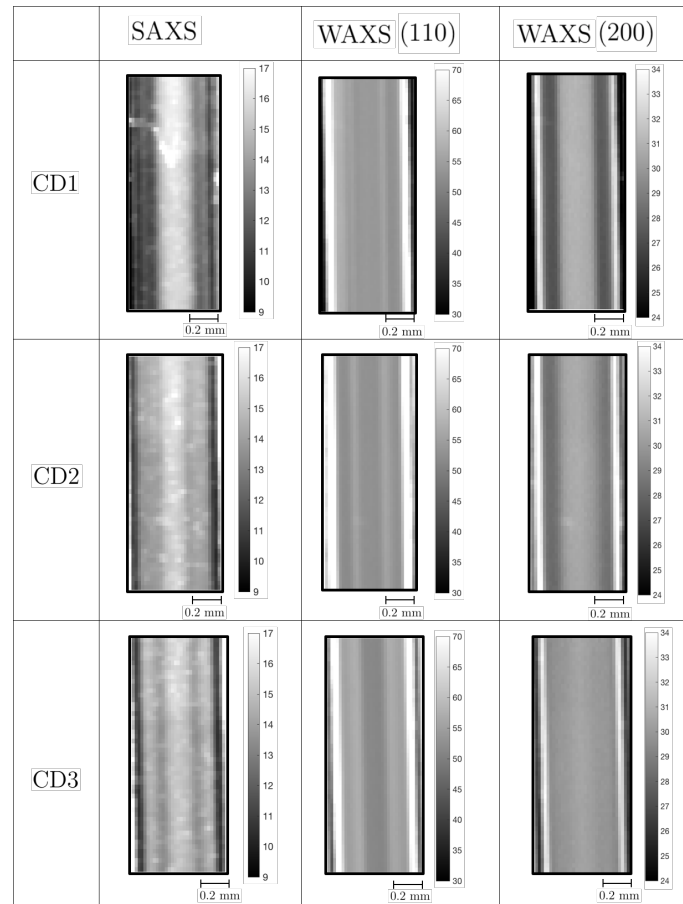


Figure 4.8: Symmetric amplitude plots taken at CD1, CD2 and CD3.

In conclusion, by comparing the scattering properties in position CD1, CD2 and CD3, it is shown that results from scanning SAXS and WAXS are highly dependent on which area of a sample that is selected. In order to fully understand why the scattering behaviour changes throughout the test plate, a deeper study of the flow pattern of the injection moulding process is needed.

Comparing Low- and Medium Viscosity LDPE

The aim by measuring two LDPE materials with different viscosity was to examine how molecular weight of the polymer, and hence viscosity, influenced the layered structure throughout the thickness. The result can be seen in Figure 4.9, where the scanning SAXS asymmetric amplitude and degree of orientation plots are shown for both medium- and low viscosity LDPE. The green and blue areas in the asymmetric amplitude plot lie outside the sample and are only included in order to compare the thickness of the skin layer. For the medium viscosity LDPE, the highly oriented skin layer consisting of shish-kebab microstructure is thicker compared to in the low viscosity LDPE. In addition, the shear layer of the medium viscosity LDPE consisting of elongated spherulites is both thicker and more ordered compared to the low viscosity LDPE.

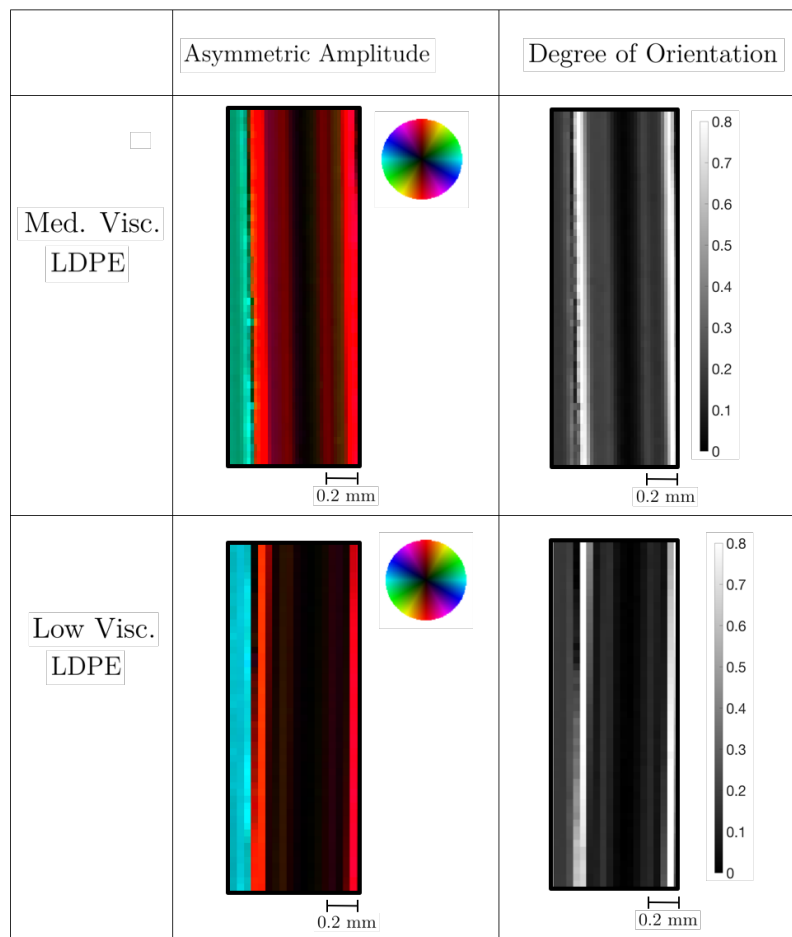


Figure 4.9: Comparison between the scanning SAXS plots of low and medium viscosity LDPE.

The difference in viscosity originates from the different molecular weights of the polymer chains, where the more viscous sample has polymer chains with higher molecular weight. Previous studies have been carried out to investigate how the molecular weight effects the microstructure of injection moulded polymers. An example is the study made by Cao et al. [7], which showed that the overall orientation

in injection moulded samples is elevated with increased molecular weight, which is in agreement with the results shown in Figure 4.9. This is explained by the assumption that polymer chain with high molecular weights are more sensitive to the flow direction than polymers with lower molecular weights.

However, other studies have also been published showing that high molecular orientations was formed in samples with lower molecular weights rather than higher ones. An example is a study of injection moulded HDPE carried out by Liu et al [6]. This study explained the phenomena with the assumption that the higher viscosity in the high molecular material gives a lower shear rate and thus a lower orientation. In short, how the molecular weight effects the microstructure of injection moulding polymers is an ongoing debate.

Even though, previous studies have shown contradicting results, it is clear from Figure 4.9 that at least for these polymers, the orientation is decreased with decreased molecular weight. However, in order to make more general conclusions, more samples need to be investigated.

Scanning SAXS of Pigmented Samples

Since scanning SAXS can be used for both transparent and opaque samples, scanning SAXS measurements were preformed for pigmented samples aiming to evaluate how the pigment effects the layered structure.

Figure 4.10 shows the symmetric amplitude plot of pigmented medium viscosity LDPE at CD1, CD2, CD3 and MD. From the figure it can be seen that the pigmented sample has a similar layered structure as the corresponding unpigmented sample, as shown in Figure 4.6 and Figure 4.8. However, as discussed in section 4.3 the pigment seem to influence the thickness of the skin- shear and bulk layer as well as the total scattering of the sample.

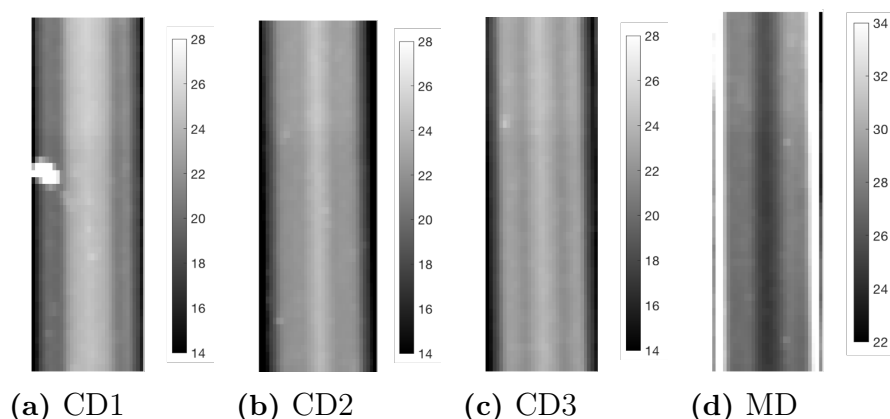


Figure 4.10: Symmetric Amplitude plot of pigmented medium viscosity LDPE.

4.4 Scanning SAXS of Deformed Samples

During the tensile testing, the dogbone-shaped samples were deformed until fracture. In order to evaluate how the microstructure is changed upon stress-strain testing, samples deformed in both MD and CD2 direction were measured with scanning SAXS and the result can be seen in Figure 4.11 and Figure 4.13

Figure 4.11a shows the asymmetric intensity plot of a top view sample deformed in the CD2 direction. The upper part of the figure corresponds to the undeformed part of the sample, and in this region the scattering patterns are aligned in the horizontal direction. This corresponds to an alignment of the polymers in the flow direction in the sample. However, in the lower part of the sample the scattering patterns are aligned in the perpendicular direction, thus the polymers in this region are oriented in the direction of the tensile stress. From this result it is obvious that the stress-strain test has not only deformed the sample macroscopically but also microscopically.

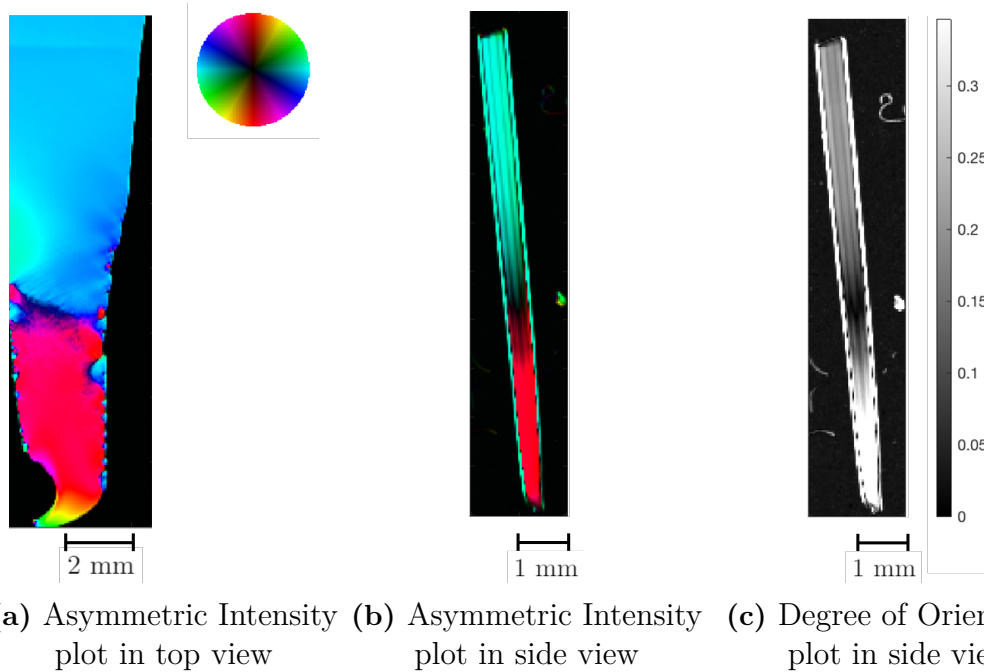


Figure 4.11: Scanning SAXS of a medium viscosity LDPE dogbone deformed in the CD2 direction.

Figure 4.11b shows the asymmetric amplitude plot in side view. The figure shows that the alignment of the skin layer is intact even in the deformed regions. Thus, the orientation of the shish kebab structure in the skin layer is unchanged when tensile stress is applied in CD. However, the structure of the elongated spherulites of the shear layer changes its orientation and the randomly oriented spherulites of the bulk layer increases its orientation in the direction of the applied force. From Figure 4.11c it can also be seen that the degree of orientation in these layers is increased. In addition, in the deformed region, no contrast between the shear and

bulk layer can be seen. Thus, after deformation, the two layers are believed to have a similar microstructure, consisting of elongated spherulites in the direction of the stress applied. Figure 4.12 shows the proposed microstructure of the sample, before and after deformation in CD.

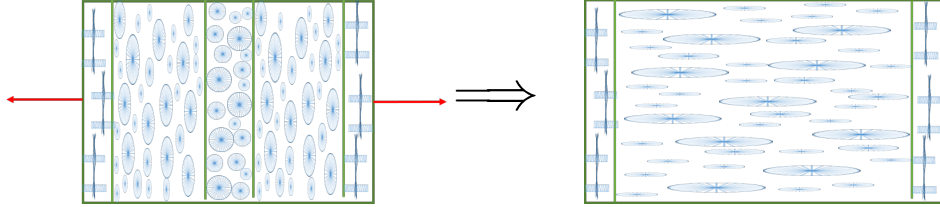


Figure 4.12: The proposed microstructure, before and after deformation in CD. The red arrows indicate the direction of the applied force.

Since the dogbone samples deformed in MD had a very small deformation region, as shown in Figure 4.4, only the very tip was measured in top view mode. Figure 4.13a shows the asymmetric intensity plot of this top view scan. From the figure only very local variations of orientation could be seen. Figures 4.13b and 4.13c show the results from the corresponding side view scans, and these figures show no change in the layered structure when approaching the fracture surface. The measurements are in agreement with the fracture process reported by Mi et al. [12], which states that when a sample that contains shish kebab microstructure is stretched in the direction of the oriented shish, the structure breaks promptly generating a crack. This crack will elongate into the shear and bulk region, causing the sample to break before the spherulites can elongate. The proposed microstructure before and after deformation in MD is shown in Figure 4.14.

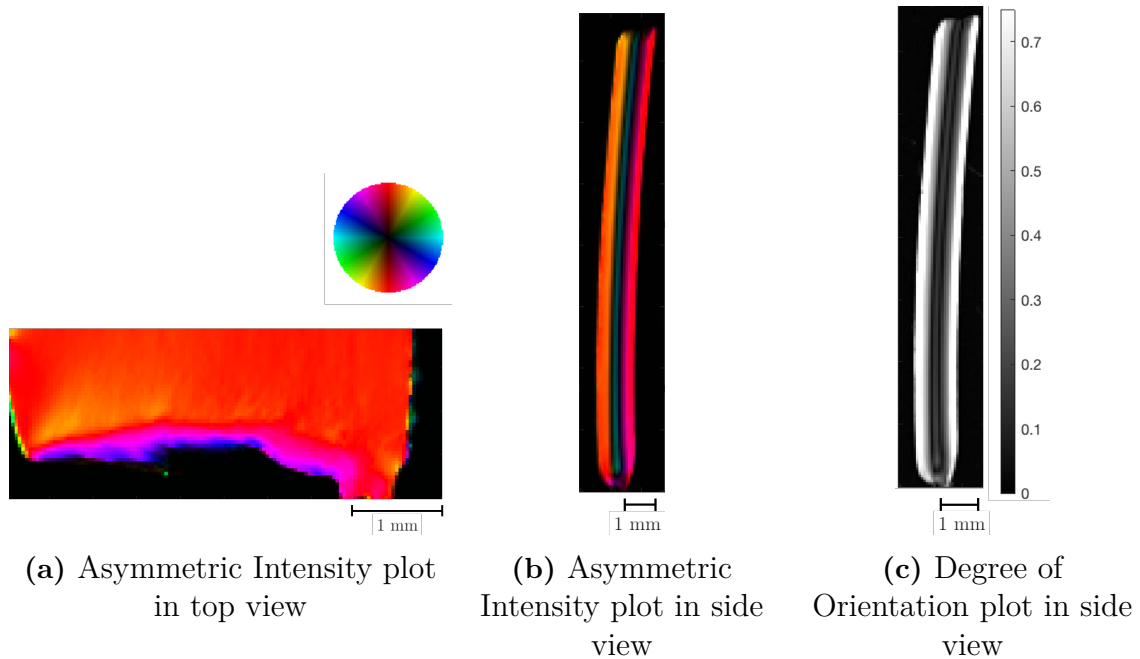


Figure 4.13: Scanning SAXS of a medium viscosity LDPE dogbone deformed in the CD2 direction.

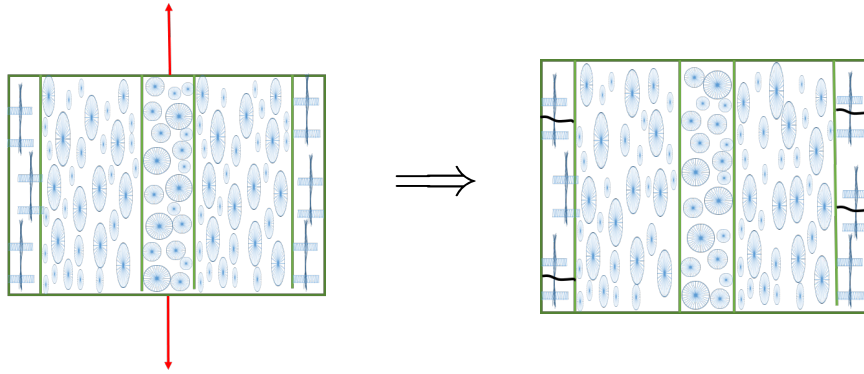


Figure 4.14: The proposed microstructure, before and after deformation in MD. The red arrows indicate the direction of the applied force, and the black stripes indicate the cracking of the shish-kebab microstructure.

4.5 Mechanical Properties

Figure 4.15 shows the tensile stress as a function of strain for low and medium viscosity LDPE without pigment. The averaged stress-strain curve of 10 samples is shown as a solid line, and the break point for each sample is shown as a dot. The figure shows that both materials are stronger in the MD direction than in the CD direction. Shish-kebab microstructure is reported to improve the tensile strength of the material, in particular in the direction of the fibril like shish [9]. Thus, the difference between material strength in MD compared to CD can be explained by the orientation of the highly oriented shish-kebab microstructure in the skin layer.

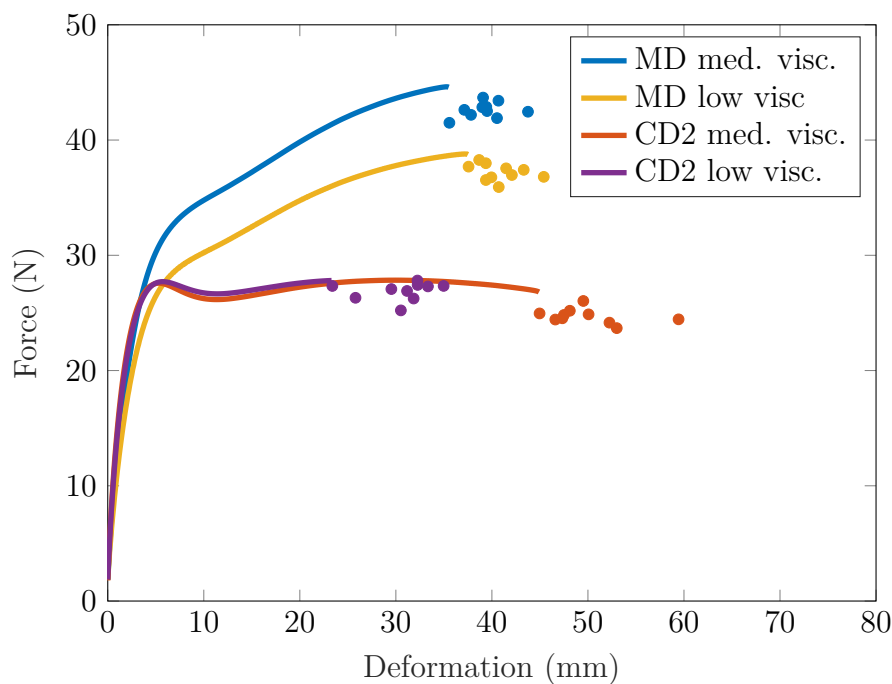


Figure 4.15: Tensile test of LDPE with different viscosities. The solid line represents the average stress/strain curve of 10 samples. The break point for each sample is shown as dots.

From Figure 4.9, it can be seen that the low viscosity LDPE has less shish-kebab structure compared to the medium viscosity LDPE. Since the shish-kebab microstructure is believed to improve the mechanical performance in MD, this would explain the higher tensile strength in medium viscosity LDPE. As shown in Figure 4.14, when stretched in MD the strong shish-kebab are believed to hold the material together, until cracks are formed in the skin layer, breaking the structure promptly. This explains why the material is less ductile in MD.

In CD, both low- and medium viscosity LDPE have almost identical yield points. Thus, the materials require the same force to be deformed. However, the medium viscosity LDPE have much higher deformation when fractured compare to the low viscosity LDPE. Further studies are needed in order to explain this behaviour.

4.6 Scanning SAXS of Commercially Available Products

Due to the complex geometry of commercially available products at Tetra Pak®, the flow pattern of the injection mould, and thereby the corresponding orientation of the polymer, can be difficult to predict. By using scanning SAXS, the orientation of the polymer through extended areas of the sample can be measured.

An example of a commercially available opening device, extensively used in Tetra Pak® packages, made from pigmented medium viscosity LDPE, is shown in Figure 4.16a. By using scanning SAXS, the area marked in red was measured in top view, and the asymmetric intensity plot of this measurement is shown in Figure 4.16b. From the left side of the sample, a thin slice was cut and measured in side view, as indicated by the dashed line in Figure 4.16a. Figure 4.16c shows the corresponding asymmetric intensity plot.

From the top view measurement, it can be seen that the preferred scattering direction changes slightly from the top (blue) to the bottom of the sample (pink/red). This indicates that the average orientation of the polymer through the sample has shifted. It can also be seen that there is a region next to the end of the screw thread with a different orientation than neighbouring areas (cyan). This is most likely a consequence of the screw thread changing the flow pattern, and consequently the average orientation of the polymer. It is shown from section 4.5 that the orientation of the polymer strongly effect the mechanical properties of the material. Thus, by identifying regions with deviating average orientation, weaker regions more prone to breakage can be determined.

From the side view scan it can be seen that the sample has a layered structure through the thickness, where the skin layer has a different orientation (pink/red) compared to the bulk (green/blue). The scattering patterns in this region indicate a shish-kebab microstructure since they show the characteristic strike in one direction and a two point pattern in the opposite direction. An example of such scattering pattern is shown to the left in Figure 4.16c. Being able to tell the amount and orientation of the shish-kebab formed is of importance, since the presence of shish kebab structure is reported to increase the mechanical performance of the material.

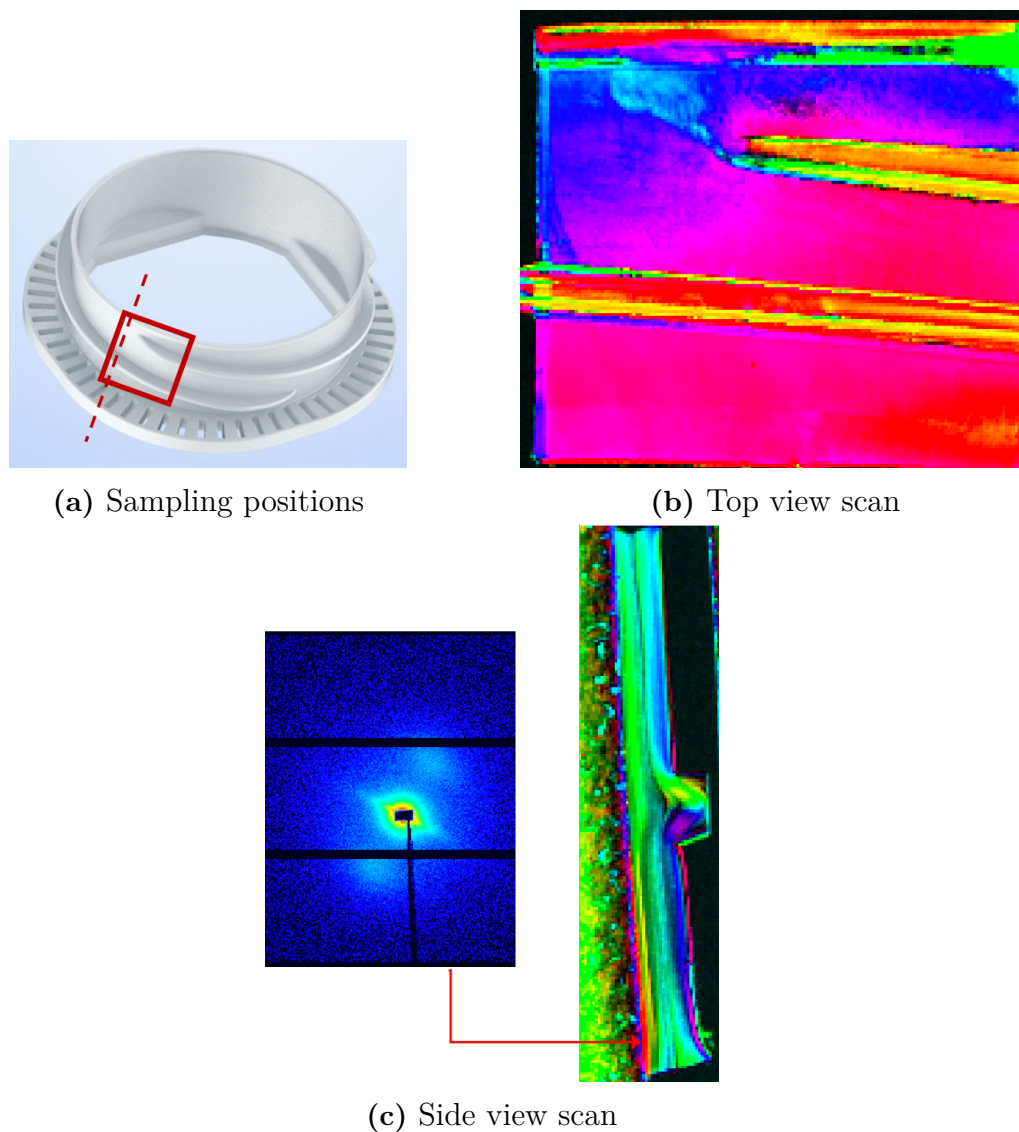


Figure 4.16: Scanning SAXS of a commercially available opening device for pigmented medium viscosity LDPE.

4.7 SEM of Deformed Samples

Aiming to further analyse the fracture behaviour of injection moulded polymers, SEM was utilised. The SEM images were taken by Daniela Nae at Material Analysis Laboratory at Tetra Pak®. Due to limitations in both time and accessibility of the SEM instrument, only samples deformed in MD were studied. Since the topography of the fractured samples was of interest, secondary electrons were used. The result can be seen in Figure 4.17

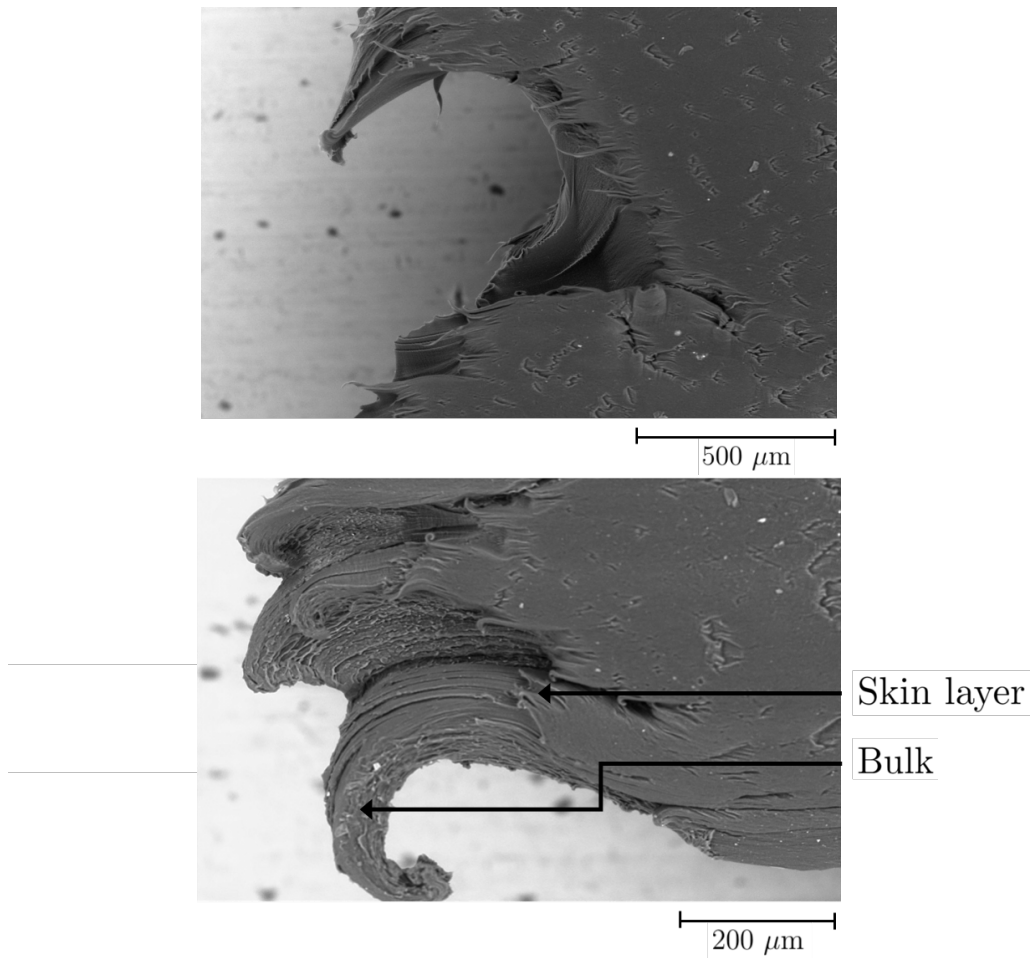


Figure 4.17: SEM images of a sample deformed in MD.

From Figure 4.17 it can be seen that the fractured skin layer has a thread like appearance. In addition, the figure shows how the bulk of the material is more deformed compared to the skin layer. This is in agreement with the fracture process proposed in Figure 4.14. However, from these SEM images it is not possible to see any differences between the bulk and the shear layer, or determine when each layer breaks.

5

Conclusions

This master's thesis has shown that SAXS and WAXS are powerful techniques for characterisation of injection moulded polymers. Compared to optical microscopy, scanning SAXS/WAXS can be used not only to visualise the layered structure of injection moulded polymers, but also to determine the microstructure of each layer and it can be used to measure both pigmented and unpigmented samples.

In this work, SAXS and WAXS data was used to propose a schematic image of the microstructure of injection moulded LDPE, consisting of highly oriented shish-kebab structures in the skin layer, intermediately oriented elongated spherulites in the shear layer and randomly oriented spherulites in the bulk layer. Furthermore, by comparing the scattering data of low and medium viscosity LDPE it was shown that the microstructure of the LDPE material investigated is noticeably influenced by the viscosity of the polymer, where the orientation was decreased with decreased viscosity.

Moreover, by using scanning SAXS/WAXS data of deformed samples, fracture processes in both CD and MD were proposed. The highly oriented skin layer is believed to give a high mechanical strength and brittle fracture in MD, while reorientation of the shear and the bulk layer is believed to give a ductile behaviour of the material in CD. The fracture processes were well in agreement with both the stress-strain curves and SEM images taken at the fracture surface.

Due to the difference of scattering behaviour in different positions of the samples, it was concluded that results from scanning SAXS/WAXS measurements are highly dependent on the area of the sample. This is believed to be a consequence of the flow pattern in the injection moulding process. In order to fully understand the link between the flow pattern and the resulting microstructure, more studies are needed.

Lastly, scanning SAXS of commercially available products at Tetra Pak® shows that the scanning SAXS/WAXS methodology is applicable for samples with complex geometries. This can be utilised for finding regions with deviating orientations and/or determine the microstructure present in various samples.

6

Future Work

This master's thesis has shown that SAXS and WAXS are powerful characterisation tools for injection moulded polymers. There are several ways to utilise the SAXS and WAXS methodology for future work, both for research- and commercial purposes at Tetra Pak.

- **Use SAXS and WAXS results for optimisation of processing parameters.** This work has shown that the molecular weight effects formation of shish-kebab structure and previous studies have shown that other process parameters such as flow rate, cooling rate and vibrations also alters the amount of shish-kebabs formed. By using these findings, the mechanical properties of the injection moulded materials could be optimised by varying the amount of shish-kebab structure introduced.
- **Quantify the influence of shish-kebab microstructure on the mechanical properties in different materials.** Previous study made by Mi et al. [12] shows that introducing vibrations during injection moulding of polypropylene increases the amount of shish-kebabs formed. By increasing the fractions of shish-kebab from 11% to 89% the tensile strength was increased from 37.9 MPa to 51.1 MPa. No studies have been found that quantify the mechanical impact of shish-kebab structure in other materials such as polyethylene.
- **Use scanning SAXS/WAXS to measure different positions of the plate in MD.** Compared to the CD direction, it has been shown that there is more contrast between the shear and the bulk layer in MD. Thus, performing scanning SAXS/WAXS in different positions of the test plate in MD would give how the bulk, shear and skin layer changes in different positions of the sample.
- **Perform scanning WAXS with full orientation of the scattering pattern.** The scanning WAXS detector used at the cSAXS beamline X12SA at SLS only covered a small angle segment. This resulted in that for the WAXS data, the asymmetric amplitude and the degree of orientation could not be evaluated. However, the shish kebab structures have highly anisotropic and

well defined scattering patterns in particular at larger angles [9]. Thus, perform a scanning WAXS with full orientation would be of interest, since it would help determining of the shish-kebab structures have twisted or untwisted lamellae.

- **SEM** Preliminary SEM studies in section 4.7 were performed for samples in MD, where it was shown that a difference in fracture behaviour of the skin layer compared to the bulk layer could be seen. Thus, it would be of interest to also examine samples deformed in CD, and compare the fracture surface of the samples. Even more information could be acquired by utilising SEM in-situ while deforming the samples, since it would show when each layer breaks. This experiment could confirm the proposed fracture processes.
- **In-situ SAXS/WAXS** Another possibility to investigate the fracture process of the samples would be to repeatably collect scattering patterns for one point in the sample while deforming it. By doing so, information of how the microstructure in that point is changing with time until breakage could be obtained.
- **Flow simulations** In order to understand how the flow pattern effect the microstructure present, deeper knowledge about the flow pattern is needed. Thus, performing a simulation of how flow pattern changes throughout the sample would be of interest since it could be used to explain the layered structure at different positions in the samples. In addition, the scanning SAXS and WAXS images taken at different positions of the test plate (see section 4.3) would be ideal to validate such simulation.

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