Influence of the Processing Conditions on Morphology and Fracture Mechanical Properties of unfilled Polyoxymethylene (POM)

Master Thesis

by

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Written at

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Leoben, June 2016

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LEOBEN, June 2016   **(Marita Halb)**

ACKNOWLEDGEMENT

KURZFASSUNG

Polyoxymethylen (POM) ist ein hochkristalliner technischer Thermoplast und wird oft in Anwendungen mit hohen Ansprüchen an das mechanische Verhalten eingesetzt. Seine Eigenschaften sind stark von der Morphologie abhängig und können durch Verarbeitung, Additive, usw. beeinflusst werden. Besonders durch die Verarbeitung kann eine weite Spanne an Eigenschaften erreicht werden.

Ziel dieser Arbeit war es, einen Zusammenhang zwischen den Verarbeitungsbedingungen, der Morphologie und den mechanischen Eigenschaften von zwei POM Typen (Delrin und Tenac) zu finden. Zu diesem Zweck wurden Platten im Pressverfahren und mittels Spritzguss mit drei verschiedenen Werkzeugwandtemperaturen hergestellt. Anschließend wurde ihre Morphologie mittels Röntgenmessungen, Polarisationsmikroskopie und DSC untersucht. Die verwendeten Röntgenmessungen können in Röntgenstreuung (SAXS) und Röntgenbeugung (WAXD) unterteilt werden, wobei die SAXS-Messungen zusätzlich auf zwei verschiedene Arten ausgewertet wurden: Einmal mittels sogenannter „1D Korrelation" und einmal mittels einem Kurvenfit basierend auf einem 3-Komponenten Modell. Ein weiteres Ziel dieser Arbeit war die praktische Implementierung und Evaluierung der verschiedenen Röntgenanalysemethoden. Die bruchmechanischen Eigenschaften der unterschiedlichen Platten wurden mittels CT-Probekörper in bruchmechanischen Ermüdungstests ermittelt. Zum Vergleich der verschiedenen Materialien wurden bruchmechanische Ermüdungskurven basierend auf vier verschiedenen Lastniveaus bestimmt.

Der höchste Kristallinitätsgrad wurde in fast allen Messverfahren bei den gepressten Platten gefunden. Sie erzielten außerdem die besten Ergebnisse in den bruchmechanischen Tests und besaßen eine sehr homogene Struktur. Die gespritzten Platten zeigten in ihrer Struktur eine starke Anhängigkeit von der Werkzeugwandtemperatur und der Probenentnahmestelle auf der Platte. Eine niedrige Werkzeugwandtemperatur führte durchschnittlich zu einer niedrigeren Kristallinität und schlechterem bruchmechanischen Verhalten. Während mittels WAXD sehr gute Ergebnisse erzielt werden konnten, lieferten hingegen die verwendeten Analysemethoden für SAXS weniger überzeugende Werte.

ABSTRACT

Polyoxymethylene (POM) is an engineering thermoplastic with a high degree of crystallinity. It is used for applications with high requirements with regard to the mechanical properties. Mechanical properties are strongly dependent on the morphological structure of the material. Through processing, additives, etc. this structure can be strongly influenced. Especially the processing conditions can vary the mechanical properties significantly.

The aim of this thesis was to find a correlation between processing conditions, morphological structure and mechanical properties for two different POM resins (Delrin and Tenac). For this purpose plates of both materials were produced using compression molding (CM) and injection molding (IM) with three different mold temperatures. The plates were analyzed concerning their morphological structure and their fracture mechanical properties. The morphological structure was determined using X-ray radiation methods, polarized light microscopy (PLM) and differential scanning calorimetry (DSC). The X-ray tests used can be subdivided into small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD). Additionally, the SAXS profiles were analyzed using two different methods: the so-called 1D correlation and a curve fitting procedure based on a 3-component model. A further aim of this thesis was the practical implementation of both, SAXS and WAXD and the evaluation of the SAXS data analysis methods (1D correlation and 3-component model) because they were not well investigated for POM. For the characterization of the fracture mechanical behavior fatigue fracture tests were performed on compact tension (CT-) specimens. Fatigue fracture curves were used for the comparison of the differently processed material plates. The curves were generated by testing at four different load levels.

The CM plates showed the highest degree of crystallinity of all plates for most test methods used. Their morphology was very homogenous even though there were big differences between the two POM resins. In the fracture mechanical tests they also revealed the best performance. The IM plates were more diverse. Low mold temperatures lead to a lower degree of crystallinity and slightly worse results in the fracture mechanical tests. The morphological structures observed using PLM varied strongly with the mold temperature and the sample position on the plate. For the X-ray tests the WAXD technique worked quite well while the results obtained from the two different SAXS analysis methods were less satisfying.

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SYMBOLS AND ABBREVIATIONS

POM	Polyoxymethylene
SAXS	Small angle X-ray scattering
WAXD	Wide angle X-ray diffraction
DSC	Differential scanning calorimetry
PLM	Polarized light microscopy
CT	Compact tension
t-POM	Trigonal POM
o-POM	Orthogonal POM
LP	Long period
FCC	Folded chain crystal
ECC	Extended chain crystal
FTIR	Fourier transformed infrared spectroscopy
TM	Tie molecules
FM	Fracture mechanics
M	Molecular weight
MWD	Molecular weight distribution
M_w	Weight-average molar mass
M_n	Number-average molar mass
D_m	Polydistpersity index
IM	Injection molding
CM	Compression molding
LEFM	Linear elastic fracture mechanics
K	Stress intensity factor

LIST OF FIGURES

1 INTRODUCTION

Polyoxymethylene (POM) is an engineering thermoplastic with a high degree of crystallinity. It is used for applications with high requirements with regard to stiffness, strength and creep behavior (Lüftl et al. 2013). These properties are strongly dependent on the morphological structure of the material and, hence, can be influenced through processing but also through additives like nucleating agents, blending, etc. However, processing is very complex and hence, can cause a very wide range of properties within one material. To create parts with the best mechanical performance possible it is necessary to know the influence of the different processing parameters on the morphological structure and the resultant mechanical behavior of the material. There is not a lot of literature for POM that deals with this topic and thus there was a need of investigation at the beginning of this work.

Aim of this thesis was to get a general idea of the influence of the processing conditions on the morphology and fracture mechanical behavior of two different POM resins. Additionally the correlation of morphology and mechanical properties was investigated. For a better understanding the corresponding scheme is illustrated in Fig. 1.1. For this purpose plates of both POM resins were produced using different processing techniques and conditions and then tested with regard to morphological structure and fracture mechanical properties. For the processing part compression molding and injection molding with three different mold temperatures were used. For morphological investigations the plates were characterized using small angle X-ray scattering (SAXS), wide angle X-ray diffraction (WAXD), polarized light microscopy (PLM) and differential scanning calorimetry (DSC). The mechanical properties were studied using linear elastic fracture mechanics (LEFM). For this cyclic fatigue fracture tests were performed to obtain fracture mechanical fatigue curves. For the fracture mechanical tests compact tension (CT-) specimens were used which were cut out of defined areas of the processed plates. For the morphological tests the plates were scanned to get an overview of the morphological state resulting from the processing and additionally, the CT-specimens were also examined in order to allow a direct correlation to the results of the fatigue fracture tests.

The results of all tests were compared to each other and a correlation between the processing conditions, the morphology and mechanical properties was deduced for the variants investigated. Since X-ray measurements (SAXS and WAXD) are not very well researched for POM some effort was put on this issue. The SAXS measurements were

analyzed with two different analysis methods and especially the evaluation of both methods was also an important point in this thesis.

Fig. 1.1: Illustration of the aim of this work

2 THEORETIC BACKGROUND

2.1 General morphology of POM

Semi-crystalline polymers are capable of forming periodic and even hierarchical structures under certain conditions. Due to limited chain mobility, variations in molecular weight and chain defects these polymers usually do not form neat crystals, so there is always an amorphous and a crystalline phase. The crystal formation and hierarchical structures depend on the polymerization process (molecular weight, molecular weight distribution, backbone, side chains, etc.), the processing of the material and its thermal and mechanical history (Michler 2016).

In the following the hierarchical composition of the crystalline phase of POM is described starting from the lowest level. POM is a linear polymer consisting of the monomer unit $[CH_2-O]_n$. The polymer chains form helical, non-chiral structures that can be separated into two polymorphic forms, the trigonal (t-POM) and orthorhombic (o-POM) one. They differ in lattice structure and conformation. The trigonal POM shows a 9/5 helical structure where nine monomer units are needed for five turns of the helix, and nine monomers of a single chain form one trigonal unit cell. In the 2/1 helical structure of the o-POM two monomers are needed for one turn of the helix and the orthorhombic unit cell consists of two chains with two monomer units each. The orthorhombic phase is not very well investigated, and is considered the 'metastable' phase that can easily be transformed into the stable trigonal phase by heating the material. A transformation from trigonal to orthorhombic phase is also possible, but has not been reported yet under standard pressure conditions. The polymorphs of POM can be detected because of their different physical properties, e. g. through wide angle x-ray diffraction (WAXD) where the different lattice constants of the crystalline systems cause different peaks in the diffraction diagrams (Lüftl et al. 2013), (Shimomura 1993). A more detailed description of crystal lattices will be given in chapter 2.3.3

The next level up in the hierarchy is the regular order of the chains and the formation of polymer crystals, respectively. The arrangement of the polymer chains usually happens in the form of lamellae with a distinct thickness and with remaining amorphous regimes in between. In this way semi-crystalline polymers reveal an alternating structures which can be described using the "long period" and the different layer thicknesses (lamellae or amorphous regime). The long period (LP) is the thickness of one repetitive constellation. In

a semi-crystalline polymer which consists of two phases only, the average thickness of one amorphous and one crystalline layer is referred to as LP.

The typical crystal formations for POM are the folded-chain crystal (FCC), the extended-chain crystal (ECC) and the shish-kebab structure. FCC is achieved by crystallization from diluted solution and consists of hexagonal-shaped lamellae. It is characterized by the chain lengths between the successive folds, which also define the thickness of the lamellae. ECC is achieved by heterogeneous cationic polymerization of trioxane. It is a needle-shaped whiskers type crystal where extended molecule chains are aligned parallel to each other (Kongkhlang et al. 2010). Shish kebab is a hybrid of ECC and FCC with several lamellae growing around a needle-shaped crystal. These different types of crystals cannot be distinguished by WAXD but by Fourier transformed infrared (FTIR) spectroscopy which has a much higher sensitivity to morphological changes (Lüftl et al. 2013). Hama and Tashiro did a more detailed research on the crystalline phases of POM crystallized from melt by cooling. Through non-isothermal X-ray measurements and FTIR spectroscopy they found that melt-crystallized POM has, unlike other polymers, FCC lamellae with no secondary lamellae but ECC stems in between. The ECC areas emerge by aligning and tautening of the tie molecules between the lamellae (Fig. 2.1) (Hama and Tashiro 2003). This is important in terms of conventional processing techniques (compression molding (CM), injection molding (IM)), which are based on cooling the melt to form a solid part.

Fig. 2.1: Development of FCC and ECC in POM during melt-crystallization (Hama and Tashiro 2003)

The highest hierarchical level of the morphology includes various crystalline structures in the size range from nanometers up to millimeters. The final structure is strongly dependent

on the crystallization conditions, foreign particles and the history of the material. Solvent crystallization for instance can lead to star and diamond shaped crystals whereas melt crystallization leads to spherulites. The latter is of prime importance for this thesis and hence described in the following. Spherulites are globular aggregates that can reach a diameter of up to 5 mm. Because of their inner structure spherulites display a typical Maltese cross under a polarized light microscope. Rod-shaped lamellar crystals grow radially from a center. The gaps between the crystalline rods are filled with amorphous chains; however branching of the lamellae is also possible. The molecule chains in the lamellae are considered to run perpendicular to the radial growing direction of the spherulites (Geil 1967), (Lüftl et al. 2013).

Besides the hierarchical structure POM shows two more morphological phenomena which are typical for semi-crystalline polymers in general and which are especially important for this work: tie molecules (TM) and entanglements. Tie molecules are molecule chains which are part of two adjacent lamellae. The part of the chain between the two lamellae acts as connection or covalent bonding. In other words it ties the lamellae together. Entanglements are kind of knots. They are chains that are physically crosslinked. Through crystallization this crosslinking gets preserved. Usually chains from adjacent lamellae are intertwined (Seguela 2005) and because of their tree dimensional arrangement they cannot be separated easily. Hence, they lead to additional strength of the material. In Fig. 2.2 the two latter morphological phenomena are illustrated. The lined areas represent crystalline lamellae and the clear area in the middle is the amorphous phase where the tie molecules and entanglements pass through.

Fig. 2.2: Illustration of a tie molecule (left) and an entanglement (right) (Seguela 2005)

2.2   Correlation between morphology and fracture mechanics

There are several morphological aspects that influence the fracture mechanical (FM) behavior of semi-crystalline polymers. The fundamental morphological parameters are the molecular weight (M) and the molecular weight distribution (MWD). For fracture behavior it was found that a high M combined with a narrow MWD improves the resistance to crack growth. This is due to the formation of tie molecules (TM) and entanglements. Long chains have a greater probability to form TM and entanglements and the force needed to resolve those TM and entanglements increases with their length as well. Also crazing is more likely at a higher M. Crazing leads to oriented fibrils of entangled molecules that emerge in load direction, stiffen the material and hence, reduce the fatigue crack propagation rate (Hertzberg and Manson 1980).

Next level in hierarchy that influences the FM behavior significantly is the crystallinity of the material. In general semi-crystalline polymers exhibit a better performance in fracture mechanical tests than amorphous polymers. According to Meinel and Peterlin this is due to the crystalline phase itself. Crystals are not only able to dissipate energy from deformation but also reform themselves to extremely strong structures (Meinel and Peterlin 1971). However, in semi-crystalline polymers most important is the connection between the crystalline regions (lamellae). The lamellae of the crystalline phase consist of long, chain folded molecules that pass back and forth within the surface of the lamellae. Lamellae are connected by Van der Waals bonding on one hand side and much more important by covalent bonding through molecule chains. There are two kinds of covalent connections: the already mentioned TM and entanglements. These bonds strongly improve the short and long term properties of semi-crystalline polymers (Seguela 2005). According to Plummer et al. the K_{IC} for crack initiation is direct proportional to the density of TM and entanglements. More entanglements can be achieved through higher cooling rates and the accompanying thinning of the lamellae to a certain grade, meaning, also the thermal history of the material influences its mechanical properties (Plummer and Menu et al. 1995).

Briefly speaking a reduction of lamellae thickness as well as an increase of molecular weight leads to an increase of TM and entanglement density and therefore to an increase in strain hardening and tensile strength. Besides that the resistance to slow crack growth, low temperature impact and creep improves with a higher number of TM (Seguela 2005).

It should be mentioned at this point that for long term properties there is one point that makes it difficult to find a direct connection between tie molecules, entanglements and the

mechanical behavior of polymers: It is known that slow crack propagation proceeds via crazing at the crack tip. The molecules at the crack tip get drawn and oriented in the direction of the applied load (Plummer et al. 1994). This leads to an additional orientation of the molecules. The former isotropic material (with defined tie molecules and entanglements) is no longer isotropic when it is passed by the crack. Crystalline lamellae get defragmented and folded chains get unfolded and taut. Hence, the mechanical behavior cannot be clearly allocated to a morphology detected in the first place. For this reason it is hard to predict the exact influence of the original tie molecule and entanglement density on the mechanical behavior of semi-crystalline materials especially concerning long term behavior (Seguela 2005).

2.3   X-ray scattering and diffraction

Material characterization using X-rays is a non-destructive method that is frequently used in crystallography. The basic principle of X-ray analyzing methods is to send a collimated X-ray beam through a specimen. The rays get scattered and diffracted by the inner structure of the material. That leads to a specific pattern which is collected by a detector on the backside of the specimen. This basic principle is illustrated in Fig. 2.3.

Fig. 2.3: Basic principle of X-ray scattering and diffraction

X-rays have a wavelength range from 0.1 to 10 nm. They are traverse electromagnetic waves just like radio waves, visible light, UV and so on. Any kind of electromagnetic wave satisfies Einstein's law of the wave-particle-duality. Both entities (wave and particle) are used in X-ray measurements to reveal separate information about the material's structure.

The particle property causes scattering of the X-ray and the wave property leads to diffraction. The results, i.e. the measured patterns of the scattered or diffracted X-rays are strongly dependent on the material and the state of the specimen with regard to stress, aggregate phase, temperature, processing history, etc. The measurement time depends mostly on the sort of X-ray radiation that is used for the tests; high energetic radiation like from a synchrotron source leads to very short measurement times of course. Also the sample thickness influences the measurement time.

2.3.1   Scattering

Scattering of electromagnetic radiation follows the typical behavior of particles and reveals structural information of the tested material in the range from 5-150 nm (Keckes 2010). The electromagnetic 'particles' are called photons. When an X-ray photon passes through matter it can interact with the electrons of the matter in two different ways: absorption and scattering. In Fig. 2.4 the possible interactions between X-ray photons and electrons are illustrated in detail. Absorption only weakens the beam but does not deliver any relevant information about the structure of the material. Hence, it will not be further discussed here. Scattering can be either elastic or inelastic. Inelastic scattered radiation passes through the specimen with a change of direction and a loss of energy (e.g. through a change in wavelength); it is also called incoherent or Compton scattering. It only contributes background noise to a scattering pattern, especially from interaction with the amorphous phase of a sample. For quantitative studies of amorphous or highly disoriented structures it is necessary to separate the inelastic from the elastic scattered parts of the curve because only the elastic part provides direct information of the inner structure of the Material (Alexander 1971). However, the material used in the present work is highly crystalline and the analyses will be of qualitative nature so there is no need to go into more detail on inelastic scattering. Elastic- (or Rayleigh-) scattering results from an interaction between the X-ray photons and the electrons of the sample accompanied with a change in direction of the photons but without a loss of energy. The electrons absorb the photons first and then become secondary emitters of photons with the same wavelength but slightly different direction compared to the incident beam (Guinier 2013). The change in direction leads to a characteristic pattern that gives information about the arrangement of the electrons within the matter (Alexander 1971).

Fig. 2.4: The four ways of interaction between X-ray photons and electrons; (A) no interaction, (B) absorption, (C) inelastic scattering, (D) elastic scattering (Jeffries, http://physics.stackexchange.com/q/150600)

If one continues this idea, it is obvious that more electrons lead to more scattering. <u>Hence, scattering can be used to measure electron densities and to characterize structures that consist of areas with different electron densities.</u>

2.3.2 Diffraction

Diffraction can be taken as evidence for the wave nature of electromagnetic radiation. Radiation gets diffracted by barriers or slits that are about the same dimension as its wavelength. Thus diffracted waves provide information about structures in the order of their wavelength e. g. X-ray radiation reveals structure information in the order of Ångström. This Phenomenon can be visualized by the well-known double-slit experiment after Thomas Young. In repetitive structures a beam is reflected / diffracted by every single layer. If a coherent beam strikes a crystal lattice and gets reflected / diffracted at different layers the reflected / diffracted beams are still coherent. When they meet again they can interfere in a constructive or destructive way. The interference pattern of a structure can be described mathematically using the well-known Bragg's Law (Eq. ((2.1)).

$$n\,\lambda = 2\,d\,sin\theta \qquad\qquad (2.1)$$

λ is the wavelength of the incidence beam, d is the lattice constant, θ is the beam's angle of incidence and n is an integer. The corresponding parameters are depicted in Fig. 2.5.

Fig. 2.5: Illustration of Bragg's Law

The diffraction pattern contains information about the crystal lattice of a material and the unit cell the crystal lattice is based on. Diffraction methods are usually used for metal powders and ceramics because of their clear lattice structure but they can also be applied to polymers. The space lattices of polymers are also built up from unit cells and hence, can be analyzed similarly. For a better understanding of the diffraction effects the basics of unit cells and reciprocal lattices will be described in the following chapter.

2.3.3   Unit cells and reciprocal lattice

To be able to interpret diffraction patterns it is important to have basic knowledge about the morphological structure of matter and especially of crystals. An important tool for the explanation of crystalline structures is the unit cell. A unit cell is the smallest repetitive unit that a space lattice is made of. Unit cells are three-dimensional structures that are defined by the length of their edges a, b, c and by the three angles α, β, γ between these edges. In the field of crystallography there are 7 basic crystal systems from which one can derive 14 Bravais lattices. They are all it needs to describe any crystal lattice possible in nature. In Table 1 the seven basic crystal systems and their main properties are summarized (Alexander 1971).

Table 1: The seven basic crystal systems

System	Edge Length	Internal Angles
Cubic	a = b = c	α = β = γ = 90
Tetragonal	a = b ≠ c	α = β = γ = 90
Monoclinic	a ≠ b ≠ c	α = β = 90 ≠ γ
Orthorhombic	a ≠ b ≠ c	α = β = γ = 90
Rhombohedral	a = b = c	α = β = γ ≠ 90
Hexagonal	a = b ≠ c	α = β = 90; γ = 120
Triclinic	a ≠ b ≠ c	α ≠ β ≠ γ ≠ 90

This system of crystal lattices works not only for metals and ceramics but also for polymers. A specialty about the polymer crystals is that a unit cell can be built from monomers of one or more molecule chains. A t-POM (trigonal POM) unit cell for example needs only one polymer chain whereas an o-POM (orthogonal POM) unit cell is built of two neighboring chains (Lüftl et al. 2013) (please refer to chapter 2.1). For the sake of completeness it has to be mentioned that the trigonal system is member of the hexagonal crystal family. Thus some authors prefer to call the 9/5 helical structure "hexagonal POM" instead of "trigonal POM".

To be able to do calculations on crystal lattices it needs more than just the Bravais lattice or the corresponding unit cell. For that purpose it is useful to introduce the so-called reciprocal lattice and the Miller indices deduced from this system. A 3-dimensional lattice can be represented on a grid with a 2-dimensional array of points like it is shown in Fig. 2.6. This grid can be divided in a set of planes with different orientations. The traces are designated by the intercepts of the corresponding connection lines on each axe. By finding these intercepts a, b, c, taking the reciprocal of each number $\frac{1}{a}$, $\frac{1}{b}$, $\frac{1}{c}$ and clearing the fraction one obtains the Miller indices h, k, l. If they are used to describe a plane they are parenthesized; e.g. (hkl) (Keckes 2010), (Alexander 1971). These Miller indices will be used later on to describe the peaks in WAXD profiles.

Fig. 2.6: Plane traces and their corresponding Miller indices on a net of space lattices
(Klug and Alexander 1976)

2.4   Linear elastic fracture mechanics (LEFM)

For the calculation of long term behavior of structural components mechanical tests are necessary. The most critical loads in these tests (among linear, static and cyclic) are cyclic fatigue loads. They lead to the quickest failure of the material. Cyclic fatigue tests can be conducted using either the stress based approach (Woehler curves) or the fracture mechanical approach. For unfilled technical thermoplastics (including POM) the fracture mechanical approach using the concept of linear elastic fracture mechanics (LEFM) was found to give good results (Arbeiter et al. 2015), (Berer et al. 2014), (Berer et al. 2015) and hence, is also used in this study.

LEFM is an effective and powerful tool for material ranking, material preselection for specific applications and for the investigation of structure-property-relationships. In comparison with other fatigue tests, LEFM offers many advantages like a reduction of testing time and number of specimens, less scattering of the obtained data and a high sensitivity to changes in the material's micro-structure. Besides that, LEFM provides material specific results on fatigue failure criteria in terms of the kinetics of fatigue crack growth independently of specimen configuration and geometry. The crack growth rate da/dN inside a material is linked to the amplitude of the so-called stress intensity factor ΔK. The stress intensity factor

K basically describes the stress field ahead of a crack tip in a linear elastic material and is dependent on the specimen geometry, load and the crack length. The same value of K at different crack tips means identical states of stress ahead of the crack tip, independently of the material and the tested geometry (Anderson 2005). LEFM in general was originally developed for materials that follow Hooke's law. Later on it was extended to materials that show linear viscoelasticity and small scale plasticity (Anderson 2005). Polymers show linear and non-linear viscoelasticity as well as hysteretic heating and history dependence of the properties. However, different authors (Lang 1984), (Hashemi and Williams 1984) worked on a concept that allows the implementation of LEFM for fatigue tests of polymers. To ensure the practical application of LEFM the following three requirements must be complied:

- The applied global stress conditions must be within the range of the linear viscoelasticity of the material
- The area of nonlinear viscoelasticity must be sufficiently small compared to the specimen dimensions
- Hysteretic heating must be confined to an area which is sufficiently small compared to the specimen dimensions

The fulfillment of the conditions cannot be generalized for all polymers but has to be checked separately for every single material, specimen geometry and load level. But even if these conditions are fulfilled there are several aspects which can influence the results of LEFM tests made on polymers. One important point in this context is the thermal and mechanical history of the material on the crack path. Each element of the uncracked bulk in the crack plane is cyclically loaded during the fatigue tests. The greater the distance between an element and the initial crack tip, the higher is the number of load cycles that the element has experienced when the crack tip arrives. This so-called far-field history surely influences the viscoelasticity and yield behavior of each element depending on its position (Lang et al. 2004). Another point is the plastic zone at the crack tip which itself can lead to material changes during the test. Crazing and shear yielding at the crack tip can cause local hardening of the material and can impede stable fatigue crack propagation (Berer et al. 2014). Thus even tests with constant values of ΔK can show variations in crack growth velocity (Lang et al. 2004). These aspects should be kept in mind when using fatigue tests based on LEFM for polymers.

By means of the load mode applied to the crack tip of the specimen one can distinguish three different types of K which are depicted in Fig. 2.7 (Anderson 2005):

- K_I: tension
- K_{II}: in-plane shear
- K_{III}: out-of-plane shear

Fig. 2.7: The three possible crack tip opening modes in fracture mechanics (Anderson 2005)

The mode considered the most critical, and also the mode used in this work, is mode I. For fatigue crack tests the amplitude of the stress intensity factor ΔK_I is used which is derived from the difference of the maximum and minimum load (F_{max} and F_{min}) of the load signal. As mentioned above K is strongly geometry dependent and for the standard compact tension (CT-) specimen (Fig. 2.8) used in this work ΔK_I is calculated according to Eq. ((2.2)) (ISO 15850), (ASTM E 647-11), (Anderson 2005).

$$\Delta K_I = \frac{F_{max}-F_{min}}{B*\sqrt{W}} * \frac{2+\frac{a}{W}}{\left(1-\frac{a}{W}\right)^{\frac{3}{2}}} * (0.886 + 4.64\frac{a}{W} - 13.32(\frac{a}{W})^2 + 14.72(\frac{a}{W})^3 - 5.6(\frac{a}{W})^4) \quad (2.2)$$

B is the thickness of the specimen, W is the specimen width and a is the initial crack length as illustrated in Fig. 2.8.

Fig. 2.8: CT-specimen geometry after the corresponding ASTM standard (ASTM E 647-11); a: crack length, W: specimen width

By plotting ΔK_I versus the corresponding number of cycles at failure for four different load levels on a half logarithmic plot one obtains a linear curve that is characteristic for the combination of material and specimen used. Requirement for the comparability of the curves is predominantly brittle failure in the same load mode for all specimens and load levels (Arbeiter et al. 2015) and of course identical environmental conditions and load ratios. The slope and the position of each curve can be used for material ranking and preselection.

3 EXPERIMENTAL DETAILS

3.1 Material

In this thesis two different resins of Polyoxymethylene (POM) homopolymer were examined. The first type was a Delrin resin produced by DuPont (DuPont, Wilmington, Delaware USA). The second one was a Tenac resin from Asahi Kasei (Asahi Kasei, Tokyo, Japan). In former tests the molecular weight and its distribution was analyzed for both materials using gel permeation chromatography (Berer et al. 2015). Additionally the polydispersity index of both materials was calculated by $Đ_M = M_w/M_n$, where M_w is the weight-average molar mass and M_n is the number-average molar mass (Aust 2014). The results are listed up in Table 2.

Table 2: Molecular parameters of the POM resins used according to (Berer et al. 2015)

Material	Weight-Average Molecular Weight M_w [g/mol]	Polydispersity index
Delrin	149,000	2.6
Tenac	137,000	2.6

3.1.1 Processing

Aim of this thesis was to find the influence of the processing conditions on various properties of POM and for this purpose both materials were processed in 4 different ways. The first variant was compression molding and the other three variants were injection molding with different mold temperatures. The main concept was to process both materials equally to make it easier to compare the direct influence of the processing conditions. Aside of minor adaptions this could generally be achieved. For all processing variants it was necessary to dry the material beforehand to get reproducible results.

3.1.1.1 Compression molding (CM)

The materials were dried in a vacuum oven at 80 °C for 3 hours. Afterwards they were stored in a desiccator. The molding press used was a Collin PCS II (Dr. COLLIN GmbH, Ebersberg, Germany). The mold used for the processing of the plates consisted of an upper and lower steel plate both covered with a sheet of Teflon to get a smooth and clean surface.

A steel frame between the steel plates acted as placeholder for the polymer. To obtain POM plates with 4 mm thickness a 4.2 mm high frame was used in order to compensate the shrinkage of the material. The inner edge lengths of the frame were 150 mm. So the dimensions of the plates were 150 x 150 x 4 mm. The corresponding processing parameters are given in Table 3 for both materials used. Both materials were processed almost identically only the heating time for Tenac had to be extended slightly. The compression temperatures are based on the materials' data sheets. The other parameter values were found empirically.

Table 3: Processing parameters used for compression molding

Delrin	Heating	Compression	Cooling
Pressure [bar]	1	100	100
Temperature [°C]	210	210	30
Time span [min]	16	15	18
Tenac			
Pressure [bar]	1	100	100
Temperature [°C]	210	210	30
Time span [min]	18	15	18

3.1.1.2 Injection molding (IM)

Before processing both materials were dried for 4 hours at 80 °C and afterwards stored in the dryer at 60 °C. The injection molding machine used was an Arburg Allrounder 470A 1000-400 Alldrive (ARBURG GmbH & Co KG, Loßburg, Germany). Since there was no injection mold with exactly the same dimensions of the compression mold the injection molded plates were slightly thicker (150 x 150 x 5 mm) than the compression molded ones (150 x 150 x 4 mm). The plates were produced with three different mold temperatures. In Table 4 the most important processing parameters are summed up for both materials.

Table 4: Processing parameters used for injection molding

	Delrin	Tenac
Metering volume [cm^3]	160	160
Volume flow [cm^3/s]	10	10
Pack pressure [bar]	600	600
Pack time [s]	12	12
Max. injection pressure [bar]	700	630
Cycle time [s]	82.8	80.8
Mold temperature [°C]	60 / 90 / 110	60 / 90 / 110

The most important processing parameters were kept constant during processing except some slight adaptions for the two different resins. Another important point was to keep the shear deformation in the mold as low as possible. Thus rather slow injection speeds were used which caused long cycle times. The cooling rates were required to be slow and well controlled which lead to high mold temperatures and a further increase in cycle times.

For all three settings (mold temperatures) and both resins filling studies were made in order to check the filling conditions in the mold. The observations were very similar in all cases and showed that the mold was filled symmetrically from the middle (Fig. 3.1). Based on this it was expected that the properties of the plates were symmetrical which was important for the definition of measurement points and sample preparation.

Fig. 3.1: Filling study of Tenac 110°C; representative for all settings / resins

3.1.2 Sample preparation

3.1.2.1 X-ray scattering and diffraction (SAXS / WAXD)

SAXS and WAXD measurements were always performed simultaneously on exactly the same spot of the specimen. Hence, for these two methods no separated sample preparation was needed. The X-ray measurements were separated in two steps. The first was a scanning of the POM plates to get an overview of the morphological state all over the plates depending on the performed processing. Here it was only necessary to cut the compression and injection molded plates into quarters so they fit into the testing chamber. In Fig. 3.2 the spots for the measurements are marked with an "x". Each measuring point was radiated and thus measured only once. No repeated measurements were performed. The plate scanning was amongst others used to verify assumptions that were made based on the processing of the plates: compression molded plates were expected to be homogenous and injection molded plates were expected to be symmetrical to the melt flow direction (refer to the filling studies in chapter 3.1.1.2). According to this the measurement points were selected in a way that the whole plate was covered taking into account the axis of symmetry. Because of significant experimental and post-processing effort the SAXS / WAXD scanning was only executed for the compression molded plates and the injection molded ones with 90 °C mold temperature.

Fig. 3.2: Measurement points used for SAXS and WAXD plate scanning; compression molded plate (left), injection molded plate (right)

The second step in the X-ray measurements was executed on the CT-specimens used for the fatigue fracture tests (details follow below). The idea was to characterize and directly

compare the morphological structure and fracture mechanical properties for each specimen. The measurement position for the X-ray measurements was about 2.5 mm ahead of the pre-milled notch of the CT-specimens. Based on previous studies (Berer et al. 2014, Berer et al. 2015) it was expected that this area was passed by the crack during fatigue crack growth. Almost all CT-specimens were tested in this way but those from the injection molded plates rotated by 90° (oriented perpendicular to the flow direction).They were expected to show the same results as the specimens which were not rotated (oriented in flow direction). For each resinl and processing condition 5 repeated measurements were conducted.

3.1.2.2 Polarized light microscopy (PLM)

Polarized light microcopy (PLM) was performed to get an idea of the microstructure of the plates (spherulite size and distribution, layer structure) and its changes along the filling direction (injection molded plates). The samples were prepared in a way that the entire thickness of the plate could be examined. They were taken from multiple positions of the molded plates which are marked in Fig. 3.3 (S stands for side and M for middle). According to the previously mentioned filling study the injection molded plates were expected to be symmetric. So there was no need to test both sides along the filling direction.

Fig. 3.3: Positions of sample preparation for PLM and DSC; compression molded plate (left), injection molded plate (right)

First the plates were cut into stripes with a buzz saw to get close to the measuring points; the injection molded plates were cut in filling direction, the compression molded plates had

no preferred direction. Then a few layers of the cut face were removed with a microtome to make the surface smooth and clean. The specimens themselves were 10 μm thick stripes that were also cut off with the microtome. These thin stripes were placed on a microscope slide and fixed with baby oil and a glass plate.

3.1.2.3 Differential scanning calorimetry (DSC)

The samples for the differential scanning calorimetry (DSC) were taken from the same plates as those for the PLM. However, only selected points were measured with DSC (from the CM plates only position M and from the IM plates positions 1S, 2S and 3S in Fig. 3.3). After preparing the samples for microscopy small pieces with 5-7 mg of weight were cut off the remaining parts of the plates with a cutter. Because each sample was intended to represent the entire thickness of the plate thin rods with 4 mm (for the compression molded plates) and 5 mm (for the injection molded plates) length, respectively were obtained. The samples were put into 40 μl aluminum crucibles and sealed with caps with two holes for pressure compensation. For each measuring position thirteen repeating tests were conducted.

3.1.2.4 Fracture mechanics

All fracture mechanics tests were performed with compact tension- (CT-) specimens according to (ASTM E 647-11). The specimens made of the compression molded plates had a thickness of 4 mm and those from the injection molded plates had a thickness of 5 mm. They were cut out of the previously processed plates with a mill cutter according to the scheme shown in Fig. 3.4. From the injection molded plates with 60 °C and 110 °C mold temperature only specimens from position 1 were made. From the injection molded plates with 90 °C mold temperature specimens from position 1 and 2 were made in order to test the difference between areas near and far from the sprue. Additionally specimens from position 1 rotated clockwise by 90 degree were made to examine the dependence of the fracture mechanical properties on the melt flow direction (in the results section these samples have the suffix Pos 1-90°rot). At least 5 specimens of each combination of position / material / processing condition were produced and analyzed using X-ray scattering and diffraction before the fatigue fracture tests. Directly before the measurements the pre-milled notch was sharpened with a razor blade to generate a defined initial crack geometry.

Fig. 3.4: Sample preparation for fracture mechanical tests – sample position in case of compression molded plate (left) and injection molded plate (right)

3.2   Methodological details of material testing and characterization

3.2.1   X-ray scattering and diffraction

The X-ray tests were performed on a Bruker NANOStar (Bruker Corporation, Massachusetts, USA). The X-ray source IμS (incoatec GmbH, Geesthach, Germany) provided monochromatic radiation with a wavelength of 1.54 Å. The X-ray beam was focused by a circular aperture with a diameter of 300 μm. In the very center of the beam a so-called "beam stop" was mounted which protected the detector from direct exposition to the beam and which guaranteed that only scattered or diffracted radiation was detected. SAXS and WAXD tests were performed simultaneously using the setup shown in Fig. 3.5. The WAXD-detector had a hole in the middle through which the scattered SAXS beam could pass. Generally, the relevant angles for WAXD analysis are way bigger than those for SAXS analysis so the WAXD patterns were not impaired by the hole in the middle of the detector.

Fig. 3.5: Setup for measuring SAXS and WAXD simultaneously

The exact distances between the samples and the detectors were determined by measuring two standards: a silver behenate standard for the SAXS detector and a silicon standard for the WAXD detector. The scattering and diffraction angles, respectively of these two materials are well known. With the measured patterns of these two materials and by using the software tool "fit2d" the exact sample to detector distance and the exact position of the beam center for both detectors could be determined. "Fit2d" is a software tool for digital image post analysis, which is provided freely by the European Synchrotron Radiation Facility (ESRF, Grenoble, France). It was used in this study for the conversion of the recorded SAXS and WAXD patterns into the corresponding profiles as described later.

All measurements were executed in vacuum with an irradiation time of one hour. A shorter irradiation time would have been possible for WAXD but not for SAXS because of the rather high thickness of the specimens (4 mm for the compression molded and 5 mm for the injection molded specimens). The type of X-ray radiation used would have led to SAXS patterns with too low contrast for the analysis when using shorter irradiation times.

The SAXS and WAXD patterns obtained are usually concentric circles. If they are elliptical or lens shaped this can be a hint for orientations in the material. The width of the rings gives information about the order quality: the sharper the edges of the rings and the thinner the rings are, the higher is the level of order. However, these two properties of the patterns

give only a very vague and qualitative idea of the morphological structure so further analysis of the patters is usually necessary. This was done by converting the 2D pattern images into 1D plots, the so-called profiles. As already mentioned above the fit2d software tool was used for this procedure. The profiles can be generated in the following two different ways:

1) Radial integration: the data points are integrated circularly for each radial point from the center to the outside according to Eq. (3.1).

$$I(q) = \int_0^{2\Pi} I(q,\chi)d\chi \tag{3.1}$$

It provides the typical SAXS or WAXD profiles which can be analyzed as described in the following chapters.

2) Azimuthal (or χ-) integration: the data points are integrated radially for each angle from 0° to 360° according to Eq. (3.2).

$$I(\chi) = \int_{q_{min}}^{q_{max}} I(q,\chi)dq \tag{3.2}$$

With this method accurate information about orientations in the specimens can be obtained.

$$q = 4\Pi * sin\frac{\theta}{\lambda} \tag{3.3}$$

In both equations q is the scattering vector and χ is the polar angle around the beam center (Alexander 1971). q is defined according to Eq. (3.3) (Hama and Tashiro 2003) where Θ is the half angle of diffraction and λ is the wavelength of the X-ray beam.

For all images both analysis methods were used and evaluated. A typical example for azimuthal integration is given in Fig. 3.6. The azimuthal profiles of SAXS and WAXD measurements are similar thus only one representative example is given. Examples for the radial integration will be given in the following chapters.

Fig. 3.6: Example for a SAXS / WAXD profile obtained by azimuthal integration

3.2.1.1 Small angle X-ray scattering (SAXS)

The recording of the measurement data was carried out automatically with a VÅNTEC-2000 2D MicroGap Detector (Bruker Corporation, Massachusetts, USA). As depicted in Fig. 3.5 the distance between the first surface of the specimen (in X-ray direction) and the SAXS detector was 1097 mm. This distance was used for calibration and analysis of the measurements in the fit2d software (alternatively the distance between the detector and the middle of the sample thickness could have been used but that would have been tricky with regard to the different sample thicknesses). According to (Alexander 1971) the small angle scattering of the X-ray radiation is caused by electron density differences in the specimen and delivers reasonable results up to a maximum scattering angle of 3°. For the profiles obtained by our measurements a maximum angle of 1.5° was already sufficient for the radial integration. A typical SAXS curve obtained by radial integration is shown in Fig. 3.7. In case of SAXS these radial integration profiles are typically illustrated by plotting the intensity over the scattering vector q (in contrast to WAXD).

Fig. 3.7: Examples of a measured SAXS pattern (left) and the corresponding 1-dimensional intensity profile obtained by radial integration (right)

The morphological interpretation of the SAXS profiles obtained was based on two different methods: the so-called "1D correlation" and a method assuming the presence of three different phases in POM ("3-component model"). One aim in this context was to get values of long period (LP) and layer thickness (a) based on both methods. In a semi-crystalline polymer the average thickness a obtained from the analysis methods used is either of the amorphous or crystalline phase, depending on the percentage of either phase. The second aim was to test the two methods and to compare them to each other on the basis of the results obtained. Both methods were implemented using "Matlab" (MathWorks Inc., Natick, Massachusetts, USA). The corresponding scripts were written and provided by my supervisor at the PCCL Dr. Michael Berer. In the following both methods will be discussed in more detail.

1D correlation

This analyzing method for SAXS measurements was introduced by (Vonk and Kortleve 1967) and examined in more detail by (Strobl and Schneider 1980). It is based on a 2-phase model assuming parallel layers of two different electron densities and an X-ray beam perpendicular to these layers. The repeating structure which is obtained in this way gives specific SAXS profiles. When conducting a Fourier transformation of these profiles the so-called "correlation function" is obtained. It contains intrinsically information about the periodicity of the structure. Using the correlation function (Strobl and Schneider 1980) developed a graphical analysis method which allows a simple determination of various structural parameters including the long period LP and the layer thickness a. This graphical analysis method was used for the analysis of the measured SAXS profiles. It was implemented in the mentioned Matlab script.

One drawback in the practical use of this method is that the entire profile down to q=0 and up to I(q)=0 is needed. In practice it is not possible to measure the entire curve and thus the measured profiles had to be extrapolated like it is shown in Fig. 3.8. The extrapolation in both sections (q to 0 and I(q) to 0) was done with functions suggested in the literature (Vonk and Kortleve 1967, Strobl and Schneider 1980). The 1D correlation in this work was conducted semi-automatically using the Matlab script.

Fig. 3.8: Schematic illustration of the extrapolation required for the analysis of the measured SAXS profiles using 1D correlation

An example of a 1D correlation curve from experimental data is shown in Fig. 3.9. The long period LP is the x-axis position of the first positive peak of the curve. The thickness a of one phase is the x-axis position of the intersection shown in Fig. 3.9. It is obtained by elongating the linear slope from the beginning of the curve to the level of the first negative peak. Whether a is the thickness of the crystalline or the amorphous phase depends on the degree of crystallinity. For a sample with more than 50% crystalline phase, a represents the thickness of the amorphous phase and vice versa (Strobl and Schneider 1980). Hence with LP, a and an expected value of the crystallinity it is possible to calculate the volumetric degree of crystallinity $X_{c,1D}$ with one of the following Eq. (3.4) a or b.

$$(a) \quad X_{c,1D,<50\%} = \frac{a}{LP} \qquad\qquad (b) \quad X_{c,1D,>50\%} = \frac{1-a}{LP} \qquad\qquad (3.4)$$

All processing techniques used in this work lead to a crystallinity of more than 50% in the POM resins examined. Thus Eq. (3.4) b ($X_{c,1D,>50\%}$) was used for the calculation of the volumetric degree of crystallinity.

Fig. 3.9: Example of a typical 1D correlation curve obtained from experimental data

1D correlation is generally based on rather simple assumptions like a 2-phase system of the material investigated. Originally these two phases are required to show a spontaneous and sharp transition in their electron densities. However, it has been shown that 1D correlation also works for more complicated structures, e.g. 2-phase systems with continuous transitions in the electron density. A material structure which is more likely for polymers. Nevertheless there are two limitations one has to keep in mind when using this method: the results obtained are only the average over the entire thickness of the specimen and superstructures limit the applicability of this method. Spherulites for example cause a superposition of two scattering effects; one from the internal partially crystalline structure of the spherulite and a second from the spherulite as enclosed structure in an amorphous surrounding. This can lead to distorted results.

3-component model

The second method used to analyze the experimental SAXS data is based on the assumption that there are 3 different morphological phases in POM at room temperature. The three

phases consist of 2 crystalline phases ("FCC" and "ECC") and an amorphous phase. For more details regarding this topic please refer to chapter 2.1. Similar to 1D correlation the input data for this method were profiles obtained by the radial integration technique but with one difference: I was transformed into Iq^2 for the correction of Lorentz factor. (Here I is again the intensity and q the scattering vector of the SAXS patterns.) A typical example for such a profile is given in Fig. 3.10. The two peaks in the profile (L_1 and L_2) are considered to come from the different crystalline phases. The first peak L_1 is related to the FCC lamellae and the second peak L_2 is related to the ECC lamellae (Hama and Tashiro 2003).

Fig. 3.10: Typical example of a Lorentz-corrected SAXS profile used as input data for the 3-component model analysis

The analysis method itself was a curve fitting procedure with the idealized 3-phase model in the background. The fitting expression was developed by (Hama and Tashiro 2003) and is based on the very fundamental scattering law given by Eq. (3.5).

$$I(q) = P(q) * L(q) \tag{3.5}$$

I(q) is the scattering intensity, P(q) is a particle factor and L(q) is a lattice factor. The latter two are complicated formulas that can be found in (Hama and Tashiro 2003) for a 2-component and 3-component model. For the curve fitting numerical optimization tools were used which are contained in the Matlab license used ("Optimization Toolbox" in combination with "Global Optimization Toolbox"). The obtained results from the curve fitting were: Δ_1 (the difference of electron density between the main crystalline phase FCC and the amorphous phase), Δ_2 (the difference of electron density between the inserted lamellae ECC and the amorphous phase), d_1 (the thickness of the main FCC lamellae), d_2 (the thickness

of the inserted ECC lamellae), σ_L (the standard error of Gaussian distribution of the lamellar periodicity) and LP (long period) (Hama and Tashiro 2003). With Eq. (3.6) it is possible to calculate the volumetric degree of crystallinity $X_{c,3comp}$ and also the volumetric percentage of FCC and ECC, respectively by setting either d1 or d2 to zero.

$$X_{c,3comp} = \frac{d_1 + d_2}{LP}$$

(3.6)

3.2.1.2 Wide angle X-ray diffraction (WAXD)

For the detection of the WAXD patterns an analog detector was used. It was placed directly in the test chamber with a distance of 49.9 mm to the sample (refer to Fig. 3.5). After every measurement it was necessary to remove the detector from the chamber, to digitize and finally delete the detected pattern before starting the next measurement. The detector was mainly sensitive to X-ray radiation but it also reacted to other kinds of electromagnetic radiation like visible light. Hence, it was important to digitize the measured pattern straight after each measurement to avoid a shading of the pattern.

After digitization the WAXD patterns were transformed into 1-dimensional intensity profiles via fit2d. Similar to the SAXS patterns this happened through the previously described radial and azimuthal integration. An example for a curve obtained from radial integration is given in Fig. 3.11. I is again the intensity and 2θ is the angle of diffraction. The latter is the main difference to the SAXS profiles in which the scattering vector q is used instead of 2θ. Both can be easily transformed into each other by using Eq. (3.3).

The interpretation of the WAXD profiles was way more straightforward than that of the SAXS profiles. As the name says the diffraction patterns result from diffraction and consist of defined Debye-Scherrer rings. Each crystalline structure leads to an explicit peak in the curve. To be precise each kind of reciprocal lattice leads to a peak and each peak can be related to the corresponding Miller indices of this reciprocal lattice.

Fig. 3.11: Example of a measured WAXD pattern (left) and the corresponding 1-dimensional intensity profile obtained by radial integration (right)

For the sake of completeness it has to be mentioned that the peaks from polymers are not as sharp as those from metals because of the less pronounced formation of the crystals and the ill-defined interfaces between the different structures. The amorphous areas lead to a characteristic halo of radiation (Alexander 1971). In Fig. 3.12 a typical WAXD profile of POM measured on a highly crystalline sample is shown (Shimomura 1993). The peaks at the different diffraction angles are accompanied by the Miller indices of the corresponding crystalline planes.

Fig. 3.12: WAXD profile of a highly crystalline POM taken from (Shimomura 1993)

For the evaluation of the WAXD profiles the areas of the peaks were normalized by relating them to the total area. The normalized area under the amorphous halo represented the mass fraction of the amorphous phase $X_{a,WAXD}$ and the sum of the normalized areas under the crystalline peaks represented the crystalline mass fraction $X_{c,WAXD}$. The procedure is mathematically expressed for $X_{c,WAXD}$ by Eq. (3.7) (m_c and m_a are the total areas under crystalline and amorphous peaks, respectively):

$$X_{c,WAXD} = \frac{m_c}{m_c + m_a} \qquad\qquad (3.7)$$

Thus using WAXD amorphous and crystalline fractions and even the different types of crystal lattices in the sample could be distinguished. However, FCC and ECC structures can generally not be distinguished using WAXD because they have the same crystal structure and thus the same diffraction pattern. To separate these two crystalline structures SAXS or Fourier transform infrared (FTIR) spectroscopy are recommended in the literature (Kongkhlang et al. 2010).

3.2.2 Polarized light microscopy (PLM)

The PLM images were acquired on an Olympus SZX12 stereo microscope (Olympus Corporation, Tokyo, Japan). The intention of this method was to qualitatively examine the microstructure of the differently processed POM plates. This comprised the spherulite size and distribution as well as the layer structure induced by the injection molding. The samples were placed between two crossed polarizers (twisted by 90°). The images were taken using the transmitted light mode. For the default magnification of 25 the exposure time was set to 100 ms. Additionally a magnification of 90 was used in combination with an exposure time of 200 ms.

3.2.3 Differential scanning calorimetry (DSC)

The DSC measurements were executed on a DSC 1 STAR^e System (Mettler-Toledo International Inc., Columbus, Ohio, USA). Before the measurements the calibration of the machine was checked with a standard iridium sample. All samples were tested using the same method. The details of the method are summed up in Table 5. The crystallinity $X_{c,DSC}$ of the samples was calculated using Eq. (3.8)

Table 5: Method used for the DSC measurements

1st Heating	Hold	Cooling	Hold	2nd Heating
25°C → 230°C	230°C	230°C → 25°C	25°C	25°C → 230°C
10°C/min	3 min	10°C/min	3 min	10°C/min

$$X_{c,DSC} = \frac{\Delta H}{\Delta H_0} * 100 \qquad\qquad (3.8)$$

ΔH_0 is the melt enthalpy of 100% crystalline POM which is 250 J/g according to (Plummer and Béguelin et al. 1995). ΔH is the measured melt enthalpy obtained from the tests. The melt enthalpy from the first heating run was used to calculate the crystallinity of the samples which will be used for comparison and interpretation later on in the results section. The temperature holding phases were implemented to allow a homogenization of the sample temperature. The second heating was done to check for differences in the material compared to the first heating run.

3.2.4 Fracture mechanical characterization

Fatigue fracture tests were selected for the fracture mechanical characterization because they are known to be very useful for material ranking (Arbeiter et al. 2015). Moreover, they were found to be very sensitive on morphological changes (Berer et al. 2015). Aim of the tests was to determine the number of cycles to crack growth initiation and to final fracture in dependence on the different load levels (ΔK_I levels) applied. This was done for both resins and all selected processing conditions (for details please refer to chapter 3.1.2.4).

The method used was based on the method suggested by (ISO 18489). In comparison to the method suggested in the standard two adaptions were made in this work. Firstly compact tension (CT-) specimens were used instead of cracked round bar (CRB-) specimens. Secondly the obtained fatigue crack growth curves were not compared with regard to slow crack growth but fatigue crack growth behavior of the material. As it is suggested in the attachment of the standard the amplitude of the stress intensity factor (ΔK) was used to express the local load level inside the specimen (ahead of the crack tip). Fracture mechanical fatigue curves (ΔK plotted over the number of cycles at failure) were used to compare the different material states. . For each material, processing condition and position variation examined one complete fracture mechanical fatigue curve was generated consisting of four points tested at different load levels.

The tests were performed on a servo-hydraulic testing machine of the type "MTS 858 horizontal" (MTS System Corporation, Minneapolis, Minnesota, USA). Right before the testing the notch of each specimen was sharpened with a razor blade to get a clearly defined initial crack geometry. The load ratio R selected was $R=F_{min}/F_{max}=0.1$ and the frequency used was 10 Hz for all measurements. A sinusoidal signal was used and all tests were conducted in load controlled mode. The four load levels used for the generation of the fracture mechanical fatigue curves (characterized by maximum and minimum load) are listed up in Table 6. The original idea was to use 50 N steps for the tests of the specimens from the injection molded plates. Unfortunately most of the test with a maximum load of 650 N lead to abrupt failure and tests with 450 N would have lasted way too long so a 25 N step was inserted between 550 and 600 N. The specimens from the compression molded plates were approximately 20 % thinner than the injection molded ones. Thus the corresponding loads were also reduced by 20 %.

For the determination of the cycles to crack growth initiation piston displacement, force and cycle number were recorded every 100 cycles. From this data the specimen compliance in dependence of the cycle number was plotted. The cycles to crack growth initiation could be determined rather simply from these plots. They were located at the first discontinuous increase in the specimen compliance.

Table 6: Load levels used for the fatigue fracture tests

Measuring point		1	2	3	4
Injection molded plates	F_{max} [N]	500	550	575	600
	F_{min} [N]	50	55	57.5	60
Compression molded plates	F_{max} [N]	400	440	460	520
	F_{min} [N]	40	44	46	52

In former tests Dr. Michael Berer had already proved that the linear elastic fracture mechanics method (LEFM) is valid for testing of POM under the given standard conditions (23°C and 50% humidity) and with the load levels used (Berer and Pinter 2013, Berer et al. 2014, Berer et al. 2015).

4 RESULTS AND DISCUSSION

From a previous study of Dr. Berer it is known that POM can show significant post processing changes when stored at room temperature (Berer et al. 2015). X-ray measurements and fracture mechanical tests are very time consuming and thus it was not possible to execute them within a short period of time. From the first to the last test about 4 months elapsed. Even though efforts were made to store all specimens protected from light and at standard climate conditions it cannot be fully excluded that post processing changes had some effects on the measured material properties. However, since in this work the materials were processed under comparatively moderate conditions (this was not the case in Berer et al. 2015) the aging effect is expected to be of minor importance. Nevertheless, it has to be kept in mind upon interpreting the results.

For a better understanding of the following discussion of the results a short explanation of the four parts of the nomenclature used is given in Fig. 4.1.

Material	Processing	Mold temperature (for IM plates)	Position on initial plate
Delrin Tenac	IM…injection molding CM…compression molding	60°C 90°C 110°C	M; 1M, 2M, 3M 1S, 2S, 3S Pos1, Pos2, Pos1_90°rot

Fig. 4.1: Explanation of the specimen and sample nomenclature used in this work

In the following this nomenclature will be used only. Some of the specimens needed just the first two or three parts to be described. In these cases the latter ones are left out.

4.1   Material morphology

4.1.1   X-ray scattering and diffraction

For both SAXS and the WAXD measurements the azimuthal integration provided curves which all indicated molecular orientations in the same direction (0°/180°). Even if the specimens were rotated by 90°, 180 or 270° the obtained orientations still pointed in 180° direction. These "orientations" of the material obviously did not come from the specimens themselves. Their origin could not be identified but it is strongly expected that they were caused by the Bruker NANOStar itself (calibration, some setup problems, etc.). Additionally, none of the scattering and diffraction patterns detected showed any obvious evidence for orientations. However, the results definitely did not represent any real orientations in the material and hence will not be further discussed here. It should be mentioned that the oscillations in the intensity levels along the azimuthal analysis path were very small compared to their magnitude. Therefore, it is assumed that the influence of this systematic error is negligible with regard to the results from the radial integration, that are discussed in the following.

4.1.1.1 SAXS

As already mentioned in section 2.3.1 SAXS provides results based on elastic scattering of X-ray radiation. Usually also inelastic scattered photons are detected. The inelastic part of the detected pattern is theoretically not allowed in the evaluation models used. It should be considered background noise and subtracted from the SAXS profiles before the evaluation of the curves (Alexander 1971). However, with the setup used it was not possible to quantitatively determine the inelastic scattered fraction of the pattern and thus it could not be subtracted from the profiles. Since the setup did not allow the determination of absolute scattering intensities but that of relative intensities only this was not a major issue in this work. However, it has to be mentioned for the sake of completeness.

1D correlation

A general shortcoming of this method is the fact that it is based on a 2-phase model. As already mentioned the morphological structure of POM is way more complicated than alternating flat layers of crystalline and amorphous structures (section 2.1). Hence, it was not clear at the beginning if this method can give acceptable results for POM at all. Thus one important point why 1D correlation analysis was carried out in this work was to check its applicability for the materials examined. Because of the questionable applicability of the

method the results obtained in this study should be interpreted rather qualitatively than quantitatively.

The method itself contains many error sources, e.g. the correct extrapolation of the measured curve on both ends with regard to the exact position and degree of the extrapolation curve; the initial slope of the correlation function which was generally not constant; the exact peak positions of the correlation function; etc. Each change in one of these parameters during the analysis leads to a more or less significant change in the results. Thus in order to obtain comparable results it was tried to keep all parameters as constant as possible. For the SAXS measurements analyzed using 1D correlation the degree of crystallinity was calculated using Eq. (3.4) b. It has to be emphasized at this point that the crystallinity obtained by this equation is the volumetric degree of crystallinity.

The results from the plate scans are given in Fig. 4.2 and Fig. 4.3. Each value given was a single measurement. The CM plates show a much higher crystallinity than the IM ones. What is interesting is that the deviation of the crystallinity is much bigger for the CM plates even though they were expected to be very homogenous. It has to be mentioned that for the scans of the CM plates the radiation times varied from 3600 to 6000 seconds. This was because these scans were conducted at the very beginning of this work. At this time the used test method had not been fully established. In accordance with the method after (Vonk and Kortleve 1967) the normalization of the correlation curve was implemented in the 1D correlation Matlab script. Hence, it was assumed that the radiation time should not have any influence on the results, as long as the number of counts of the pattern is within a certain range. However, it seems that the radiation time does have an influence. Alternatively, it is also possible that the discussed effect resulted from the error-prone analysis method as mentioned above.

Fig. 4.2: Crystallinity of plates scanned with SAXS and analyzed using 1D correlation
(Delrin_CM (left) and Delrin_IM_90°C-MT (right))

Fig. 4.3: Crystallinity of plates scanned with SAXS and analyzed using 1D correlation
(Tenac_CM (left) and Tenac_IM_90°C-MT (right))

In the following the results for the CT-specimens are discussed. For each processing / material variant investigated five repeated measurements were conducted. The average values of the LP and the layer thickness a (of the amorphous phase) which were subsequently used for the crystallinity calculations are given in Table 7. The corresponding crystallinity values are shown in Fig. 4.4. It is obvious that the CT-specimens made of CM plates showed the highest crystallinity and the crystallinity of Delrin_IM specimens was generally higher than of Tenac_IM. This was expected from the processing conditions because of the much longer cooling time in case of CM which gives the material more time

to crystallize. For the IM specimens a slight shift to higher crystallinity can be noticed towards higher mold temperatures. This shift could also result from longer cooling times and from the smaller temperature difference between melt and mold. However, it has to be kept in mind that the standard deviations of the average values are about the same order as the differences in the crystallinity values between the different mold temperatures.

Table 7: Long period and layer thickness obtained for the CT-specimens using 1D correlation (values were subsequently used for the calculation of the degree of crystallinity)

Specimen	LP [nm]	a [nm]
Delrin_CM	17.20	3.96
Delrin_IM_60°C-MT	14.36	4.12
Delrin_IM_90°C-MT_Pos1	15.36	4.30
Delrin_IM_90°C-MT_Pos2	14.96	4.08
Delrin_IM_110°C-MT	16.44	4.44
Tenac_CM	16.54	3.80
Tenac_IM_60°C-MT	14.20	4.34
Tenac_IM_90°C-MT_Pos1	14.82	4.52
Tenac_IM_90°C-MT_Pos2	14.92	4.54
Tenac_IM_110°C-MT	15.68	4.70

Fig. 4.4: SAXS degrees of crystallinity for CT-specimens made of Delrin (left) and Tenac (right) obtained by 1D correlation

3-component model

Similar to the 1D correlation method the 3-component model is based on an idealized model with well-defined borders between the phases. However, this model was developed especially for POM (Hama and Tashiro 2003, 2003, 2003) and thus it was expected to give quite good results. According to (Hama and Tashiro 2003, 2003, 2003) SAXS profiles of POM usually show two peaks which are each related to one of the different two crystalline lamellae (Fig. 3.10). Representative profiles from this study are illustrated in Fig. 4.5. It was tried to fit these curves with the fitting functions suggested by (Hama and Tashiro 2003). However, by fitting the curves using the given formulas it was not possible to match the measured and the calculated curve perfectly. The position of the second peak was badly reproduced by the model, especially for Delrin_CM. But also the exact shape and height of both peaks could hardly be fitted using the 3-component model. Another issue was the slope at the end of the curves. This slope is an inherent property of the fitting function. It can also be observed in the studies by Hama and Tashiro (Hama and Tashiro 2003) when using the given parameters and extending the x-axis of the profile plot to 1.5 nm^{-1}. Its influence on the obtained results is not known at this point. Despite the obvious shortcomings, the analysis was performed and the results are given and discussed in the following.

Fig. 4.5: Examples of SAXS profiles determined in this work with the corresponding curve fits generated using the 3-component model (left: Tenac_IM; right: Delrin_CM)

In the following the results of the plate scans analyzed with the 3-component model are discussed. For the plates only the (volumetric) degree of crystallinity is presented (Fig. 4.6 and Fig. 4.7). Delrin_CM had the highest degree of crystallinity followed by Tenac_CM and the IM specimens. The deviation of the degree of (volumetric) crystallinity is about 1 % for

Delrin_IM, Tenac_CM and Tenac_IM which is very low especially for the IM plates. Surprisingly also Delrin_CM showed small differences all over the plate. This is completely different to the corresponding results obtained using 1D correlation. There rather big differences were found. As already mentioned before the differences are very likely to be related to experimental details (e.g. radiation times) or the error-proneness of the 1D correlation method. With the current results it is now unclear if the previously observed differences were introduced by the 1D correlation method, or if the 3-component method is not sensitive enough to resolve them. The latter is supported by the very narrow distribution observed for the other plates when using the 3-component model. As already mentioned it was not possible to fit the measured curves perfectly. Thus the curves which were "the closest" to the measured ones were taken for the results. The "closest" curves were found by the Matlab script used through "least squares optimization" and a local and global minimum search algorithm. They were sometimes quite far from the measured curves but very similar to each other and hence, lead to very similar results. For Delrin_CM in particular there were some further problems with the obtained fitting curves: it was not possible to fit the position of the second peak to the measured curve. All together the consistency of the crystallinities within the different plates seems to be an effect of the analysis method (3-component model).

Fig. 4.6: Crystallinity of plates scanned with SAXS and analyzed using the 3-component model (Delrin_CM (left) and Delrin_IM_90°C-MT (right))

Fig. 4.7: Crystallinity of plates scanned with SAXS and analyzed using the 3-component model (Tenac_CM (left) and Tenac_IM_90°C-MT (right))

For the discussion of the CT-specimen a phase distinction (FCC, ECC, amorphous) was made additionally. In Table 8 the evaluated values of the LP and the layer thicknesses of FCC and ECC are listed up for Delrin and Tenac. The values are averages of 5 analyzed specimens each. The corresponding crystallinities (volumetric degree) with the crystalline phase separated into FCC and ECC are shown in Fig. 4.8 and Fig. 4.9. There are no error bars given because the standard deviation was less than 1 % for all variants measured. Aside from the deviation of the scanned Delrin_CM plates it can be seen that the results of the CT-specimens are in very good correlation with those from the scanned plates. Delrin_CM has a very high percentage of ECC and an average crystallinity of 84% which is significantly higher than for all the other variants. This is in good correlation with the theory of the origin of the ECC phase. ECCs are interpreted as a result of the growth of crystalline lamellae during the crystallization process. Through the apposition of new lamellae to the crystallites (spherulites) the amorphous molecules in between are stretched and finally form bundles of taut molecule chains. Since Delrin is communicated to contain high contents of nucleation agent many nucleation centers and thus small spherulites are obtained (refer to section 4.1.3). Due to the resulting high density of spherulites it is anticipated that the amorphous layers between the lamellae are more stretched and more ECC lamellae are generated. The higher degree of crystallinity compared to the IM samples is attributed to the very slow and controlled cooling rate at CM.

Tenac_CM also has a slightly higher degree of crystallinity compared to Tenac_IM specimens but here is no higher content of ECC lamellae observed. The smaller number

and bigger size of the spherulites is speculated to be the explanation for this. The amorphous areas between the lamellae are expected to be bigger and thus the molecules in this area are less stretched. Additionally the probability for one molecule chain to be in two adjacent lamellae is lower.

The IM specimens of both materials show a slight increase in FCC and ECC from low to high mold temperatures. The general level of crystallization in IM can be considered very similar for Delrin and Tenac.

Table 8: Long period and layer thicknesses of FCC and ECC phases used for the subsequent calculation of the degree of crystallinity (CT-specimens)

Specimen	LP [nm]	d_1 [nm]	d_2 [nm]
Delrin_CM	11.30	7.48	2.01
Delrin_IM_60°C-MT	10.97	7.17	0.94
Delrin_IM_90°C-MT_Pos1	11.14	7.42	1.06
Delrin_IM_90°C-MT_Pos2	11.14	7.40	1.06
Delrin_IM_110°C-MT	11.27	7.54	1.15
Tenac_CM	11.25	7.54	1.16
Tenac_IM_60°C-MT	11.01	7.20	0.92
Tenac_IM_90°C-MT_Pos1	11.14	7.43	1.03
Tenac_IM_90°C-MT_Pos2	11.15	7.44	1.04
Tenac_IM_110°C-MT	11.24	7.55	1.11

Fig. 4.8: Distribution of FCC, ECC and the amorphous fraction in Delrin CT-specimens (SAXS measurements analyzed with 3-component model)

Fig. 4.9: Distribution of FCC, ECC and the amorphous fraction in Tenac CT-specimens (SAXS measurements analyzed with 3-component model)

Comparison 1D correlation - 3-component model

Both methods showed the highest (volumetric) degree of crystallinity for the CM plates and an increase in crystallinity for the IM plates from low to high mold temperatures. This leads to the conclusion that it is possible to get qualitatively useful results from both methods. However, the quantitative values were different and should generally be treated with caution. As a summary one can say that too many assumptions are included in both models which simply cannot be fulfilled by technical POM materials. Nevertheless it has to be repeated at this point that the 3-component model was especially developed for POM and

it worked quite well for POM materials with lower molecular weight (Hama and Tashiro 2003). The 1D correlation method on the other hand was already successfully tested on other polymers than POM (Strobl and Schneider 1980) and therefore can be useful in adequate applications. Interestingly, despite these shortcomings the differences in the crystallinities are rather small. The comparison of the calculated long periods shows higher deviations. While 1D correlation gives a range of LP from 14.20 nm to 17.20 nm the 3-component model gives LPs between 10.92 nm and 11.30 nm. Thus the 3-component model leads to about 30 % shorter LPs than 1D correlation.

On the search for alternatives to these two SAXS analysis methods a more fundamental physical theory about the origin and the position of the peaks with regard to the inner structure of matter was also considered. It says that two (or more) peaks result from first, second (and so on) order scattering of the radiation by the same structure instead of different structures like FCC and ECC. Depending on the peak position (difference between the q-positions in [nm^{-1}]) one can derive the shape of the crystallites (q-ratio of 2 comes from flat layers, q-ratio of $\sqrt{3}$ means rod shaped crystallites, etc.). The implementation and study of these aspects has not been conducted yet because it went beyond the scope of this work but its implementation is intended in the close future.

4.1.1.2 WAXD

In Fig. 4.10 an experimentally determined WAXD profile is plotted exemplarily. The different diffraction peak ratios which were used to calculate the contribution from the lattice planes are represented by the areas under the peaks of the measured profiles. The shapes of the measured profiles were similar to those from literature. However, the peak positions were not exactly the same but slightly shifted. This is attributed to the calibration and the fact that the structures analyzed in the literature were usually rather well-defined crystals unlike the structures used in this work. Another issue which occurred in the measurements was some kind of background noise (red halo in Fig. 4.10). The origin of this halo is not clarified yet especially since no information about it was found in the literature. It is speculated that it is an effect of the specimen shape, the surface or some particles in the testing chamber. However, based on the practical observations it is expected that this halo does not influence the results significantly. In the data analysis the halo was just subtracted from the profile and the areas of the remaining peaks were used for the subsequent calculations.

Fig. 4.10: Diffraction peaks and their origin

Similar to the SAXS results only the total degree of crystallinity (mass fraction) is given for the plate scanning (illustrated in Fig. 4.11 and Fig. 4.12). The values for the different fractions are very similar to those of the CT specimens which will be analyzed in more detail later. The only fraction which varied noticeable within one plate was the peak of the (100) lattice plane. Thus the observed changes in crystallinity were mainly related to changes in the intensity of this peak.

Delrin_CM shows a deviation of about 2 % in crystallinity which is a lot compared to the results from the CT-specimens but very few compared to the other scanned plates. The total crystallinity of Tenac_CM varies by 3.6 %. For Delrin_IM the deviation is almost 10 % and 15 % for Tenac_IM. The smaller deviation of Delrin is attributed to a more regular crystalline structure resulting from the high content of nucleation agent (heterogeneous nucleation). The larger spherulites of Tenac which were at least partially formed by homogenous nucleation are expected to be less regular.

For the IM plates it was expected to see a decrease of crystallinity from near the sprue to far from the sprue as it is usual for injection molding. Delrin_IM shows that trend quite well while Tenac_IM seems to have just a messy structure without any obvious trends. It is anticipated that this is also an effect of the different nucleation. Because of the heterogeneous nucleation Delrin is assumed to react stronger on small temperature differences than Tenac.

Fig. 4.11: Crystallinity of plates scanned with WAXD (Delrin_CM (left) and Delrin_IM_90°C-MT (right))

Fig. 4.12: Crystallinity of plates scanned with WAXD (Tenac_CM (left) and Tenac_IM_90°C-MT (right))

With regard to the WAXD tests of the CT specimens one additional issue came apparent. Even though the testing spot was 2.5 mm away from the notch and the diameter of the X-ray beam is only 300 µm the notch was visible on the detector as shown in Fig. 4.13. The black triangle on the left side in Fig. 4.13 is the shadow of the notch. This part of the pattern was omitted in the data analysis and thus it was not a big problem for the current work. Nevertheless, for the testing of very small samples this could become a severe problem. Each edge can then lead to a shadow which distorts the WAXD pattern. To solve this

problem it is suggested to work with a metal aperture or any other kind of metal shield which blocks most of the radiation but the main X-ray beam.

Fig. 4.13: WAXD pattern of a CT-specimen showing the shadow of the notch

In Fig. 4.14 and Fig. 4.15 the results of the CT-specimens are shown. The values represent the average of 5 investigated specimens. The standard deviation of the total crystallinities was less than 1 % for the whole measurement series, which is way less than for the scanned plates. Because of the small value no error bars are included in the figures. Both materials showed an increased fraction of the (115) lattice plane of the CM specimens. The IM specimens on the other hand were all about the same level concerning their (115) peaks. Generally a higher intensity of higher located peaks indicates a more perfect order in the crystalline areas. For both materials the highest total crystallinity was found for the 90°C-MT_Pos2 specimens, but the differences were small. Nevertheless, it can be said that the total crystallinity (mass fraction) of Delrin was slightly higher than that of Tenac even though the fraction of the (105) lattice plane of Tenac is slightly increased. To sum up, the diffraction peak which dominates the degree of crystallinity is the one of the (100) lattice plane but the detailed distribution of the peaks varies with material and processing. In this work the differences between materials and processing variants are small which was rather unexpected. Originally a bigger difference was intended. To achieve this goal it is obviously necessary to process the materials with harsher processing parameters (not only changes

in mold temperature but also injecting speed, pressure, etc.). With bigger differences in the morphology it would also be easier to draw conclusions concerning the correlation of processing conditions and morphological structure.

Fig. 4.14: WAXD profile of Delrin CT specimens illustrated in form of the peak fractions of the main peaks

Fig. 4.15: WAXD profile of Tenac CT specimens illustrated in form of the peak fractions of the main peaks

4.1.2 DSC

The results from the DSC measurements are given in Fig. 4.16. For each measuring point thirteen samples were tested. The scatter in the results is much bigger than for the X-ray measurements and thus the error bars are included in the diagrams. As described in the sample preparation section (chapter 3.1.2) the samples were taken directly from the plates. Because of the different preparation technique the sample positions were different to the measurement positions in the X-ray plate scans.

Like the SAXS methods the DSC measurements also show an increased crystallinity (mass fraction) for Delrin_CM and Tenac_CM. Also here the degree of crystallinity is higher for

Delrin than for Tenac which is in good correlation with all X-ray results. A crystallinity trend from near to the sprue to far from the sprue is not indicated by the results. When considering the error bars it is obvious that the difference in crystallinity of the IM tests is smaller than the measurement scatter.

Fig. 4.16: Degree of crystallinity of Delrin (left) and Tenac (right) plates measured by DSC

The DSC measurements were only included in this work for the sake of completeness. The advantages of this method are its easy use and the fast availability of results. Nevertheless, the method has significant intrinsic shortcomings which are represented by systematic errors like material recrystallization during the heating process (Kong, Hay 2002, Blundell, Osborn 1983). This always leads to the question if the measured crystallinity is identical to the structure obtained from processing. Hence, one should not take the results from DSC measurements as absolute quantitative values especially when using them for comparison with other methods (e.g. WAXD).

4.1.3   Polarized light microscopy (PLM)

In this section an overview of the cross-section microstructures of the CM and IM plates is given. All images were obtained using polarized light microscopy. They allow a qualitative study of spherulite size, distribution and of the skin-core layer structure in the plates. In the first part the microstructure of the CM plates is discussed (representative images are presented in Fig. 4.17) followed by the discussion of the characteristics of the IM plates including representative images for Delrin (Fig. 4.19, Fig. 4.20) and Tenac (Fig. 4.22, Fig. 4.23), respectively.

Fig. 4.17: PLM images taken from CM plates; Delrin (left), Tenac (right)

In the CM plate Delrin (Fig. 4.17 left) has a very fine and homogenous structure over the entire thickness due to the high content of nucleation agent. Even with the maximum magnification of 90 it was not possible to find any changes in the structure close to the surface. Obviously Delrin does not form a skin layer when processed by CM, at least under the processing conditions used. There are some fuzzy areas which are distributed irregularly over the plate. They seem to contain even finer crystallites than the rest of the material. Their source has not yet been identified clearly but they are assumed to represent the transition between two adjacent granulate grains.

Obviously the CM plate of Tenac (Fig. 4.17 right) has a much coarser structure than Delrin and a distinct skin layer. In Fig. 4.18 the upper edge of the sample is shown with a magnification of 90. It can be seen that there is a distinct microstructure. This structure changes in direction perpendicular to the surface. While at the outermost area no spherulites can be observed they are distorted in the next section before they become spherical. It is speculated that this results from crystal growth from the cooled surface towards the hot middle of the POM plate. While at the outermost area the growth of big spherulites is inhibited by too high undercooling of the melt, in the next section the undercooling is high enough to cause nucleation but small enough to allow crystal growth. From the surface towards the center, the undercooling decreases while the spherulite size increases (little number of nucleation centers and good crystal growth conditions). What is not understood yet is why the surface effect appears for CM plates where the cooling rate is rather small and why the spherulites become finer again towards the very center of the plates. The latter is even more distinct in the IM plates and will be discussed in more detail in the appropriate section (below). After a depth of about 0.15 mm the spherulites have a

quite regular shape. Because of the long processing time and the slow cooling the spherulites had a lot of time to grow and reached an average size of 0.22 mm. The black dots in the middle section of the sample (Fig. 4.17 right) are about this size and they are very likely to be holes. They are either blowholes or spherulites which got torn out of the bulk material during the microtome cutting of the samples.

Fig. 4.18: PLM image of the skin layer of a Tenac_CM plate made with a magnification of 90

The structures of the IM plates were found to be more complex than those in the CM plates. In Fig. 4.19, Fig. 4.20, Fig. 4.22 and Fig. 4.23 exemplary images of IM samples are presented. The header row of each figure indicates the sample position (please refer to chapter 3.1.2 for more details). Each image row consists of three images taken along the plate from near the sprue to far from the sprue. The filling direction is always from the left to the right. In the upper left corner of each image row the corresponding mold temperature is indicated.

Liparoti et al. determined a general structure for injection molded Polypropylene plates which consists of the following three layers starting from the outside (Liparoti et al. 2015):

- A skin layer with two phases: at the very outside is a thin film with particular elongated structures aligned to the mold surface; and a thin interconnected structure with globular nano-structure inclusions adjacent to the previous one
- A shear layer with structures aligned along the flow direction
- And a spherulitic layer in the central zone of the plate

The study of Liparoti et al. is the most elaborated one concerning the layer structure of unfilled and injection molded semi-crystalline thermoplastics. Although it was conducted for

an alternative material (Polypropylene) it will be used as reference in this work. What is apparent in Fig. 4.19 and Fig. 4.20 is the fact that for Delrin the number of layers decreases from low to high mold temperature and from near the sprue (left) to far from the sprue (right). With regard to the layer pattern the samples from the middle section of the plates seem to be slightly more homogenous than the ones from the side section. For Delrin the layer structures shown in the images do not correlate well with the structure Liparoti et.al suggested for IM plates of Polypropylene. Hence, for Delrin it is obviously not useful to determine the layer thicknesses in accordance with Liparoti et.al. The origin of the complicated layer structure observed for Delrin is not yet completely understood. The competing mechanisms are probably shearing and nucleation. However, it seems that the bigger the temperature difference between the mold and the melt the more structural layers appear. This can also be used to explain the dependence of the layer structure on the distance to the sprue. Near the sprue the temperature difference between the melt and the mold is the biggest and it decreases the further from the sprue the melt flows. Consequently the bigger the distance to the sprue, the more homogenous the material becomes.

Besides numerous thinner layers there are three main layers which can be distinguished (especially for the samples with high mold temperature and far from the sprue): the outer layers (upper and lower side) of about 1 mm thickness and the layer in the center with a thickness of 2 mm. In Fig. 4.21 two representative images of surface layer (left) and center layer (right) of Delrin_IM_90°C-MT_S1 are shown with a magnification of 90. There is neither an obvious change in spherulite size and distribution nor in the orientation as far as this can be evaluated using PLM.

Fig. 4.19: PLM images of the cross-section of IM plates of Delrin: side position "S"; from near the sprue (left) to far from the sprue (right)

For the sake of completeness it has to be mentioned that some white lines in the images like the ones in the middle of specimen Delrin_IM_90°C-MT_S2 and _S3 come from sample preparation (microtome knife) and not from processing. Also the small black dots and bubbles in some images are not a results from injection molding but dust particles and entrapped air.

To get a more detailed idea about the exact structure of the different layers in the Delrin_IM plates, further investigation is necessary. It is suggested to use samples from single layers to obtain more information. Also the usage of different testing methods like FTIR is expected to provide further information.

Fig. 4.20: PLM images of the cross-section of IM plates of Delrin: middle position "M";
from near the sprue (left) to far from the sprue (right)

Fig. 4.21: PLM images of the skin layer (left) and the central layer (right) of
Delrin_IM_90°C-MT_S1 recorded with a magnification of 90

S1	S2	S3

Fig. 4.22: PLM images of the cross-section of IM plates of Tenac: side position "S"; from near the sprue (left) to far from the sprue (right)

The images of Tenac IM samples in Fig. 4.22 and Fig. 4.23 show much more diversity in the structure than Delrin. For some samples it is even possible to identify the layers according to the layer structure of injection molded plates suggested by (Liparoti et al. 2015). Especially in the images of the side positions ("S") the layers can be seen clearly for the lower mold temperatures. In Fig. 4.24 a representative image of Tenac_IM_90°C-MT_S1 with the marked layers is given. They even seem to match the structure details described in the literature. For the samples made with higher mold temperatures the shear layer seems to be split up in sublayers. The reason for it might be the same as for the numerous layers of the Delrin IM samples. Far from the sprue the shear layers almost disappear.

What is interesting to notice is the fact that the spherulite size obviously increases from near the sprue to far from the sprue and from the plate center to the shear layer. This is in sharp contrast to the theory of formation and growth of spherulites in injection molded plates over the thickness. Usually it is expected that spherulites grow faster and become bigger in slowly cooled areas. As the center near to the sprue is the hottest part of the plate during IM and of course the part that cools down the slowest (due to the low thermal conductivity of the surrounding material) the biggest spherulites should be found there. The spherulites size in Tenac is the exact other way around. A useful reason for this effect cannot be given at this point but it should be mentioned that a similar structure was also found for the IM CT-specimens used in two previous studies (Berer et al. 2014, Berer et al. 2015).

Fig. 4.23: PLM images of the cross-section of IM plates of Tenac: middle position "M"; from near the sprue (left) to far from the sprue (right)

Fig. 4.24: PLM image of Tenac_IM_90°C-MT_S1 recorded with a magnification of 90; layer classification in accordance with (Liparoti et al. 2015).

4.1.4 Comparison of the crystallinity obtained from the different characterization methods

A direct comparison of the degree of crystallinity obtained from SAXS and WAXD is not possible. SAXS provides a volumetric fraction and structural information in the dimension of up to 150 nm. Crystallinity information obtained from WAXD is a mass fraction and based on structures of the dimension of a few Ångström. Generally it is possible to convert mass fractions into volumetric fractions and vice versa but that does not make sense in this context. The methods used for the analysis of the SAXS data were quite sophisticated but not very appropriate for POM. Hence, there is potential for improvement. Nevertheless, all X-ray methods showed similar trends in the degree of crystallinity. The CM specimens showed the highest crystallinity and the IM specimens revealed an increase in crystallinity from low to high mold temperature. Some small exceptions were found in the WAXD results. There the specimen Delrin_IM_90°C-MT_Pos2 had the highest degree of crystallinity.

The DSC measurements also reflected the finding that the CM specimens had the highest crystallinity. No significant trends in the degree of crystallinity along the filling direction of the IM plates were detected by the DSC measurements because the differences were within the experimental scatter.

However, structural changes along the filling direction of the IM plates could be seen in the PLM images. Also the influence of the mold temperature was made visible with that method. The direct correlation of PLM images and the results from the X-ray analysis is difficult. Firstly, because the measured structures from the X-ray methods are much smaller than what can be seen with an ordinary light microscope. Secondly, because the results from

the X-ray methods are average values over the entire thickness. To improve comparability X-ray investigations of thin layers perpendicular to the plate thickness should be included in the examinations. This might also give more information about the structure of each layer with regard to orientations, distribution of diffraction peaks, etc. Particularly for Delrin it would be interesting to see if X-ray analysis can resolve any significant differences between the numerous layers observed in the PLM images.

4.2 Fracture mechanical characterization

In Fig. 4.25 and Fig. 4.26 the results of the fatigue fracture tests are summed up for both materials and all processing conditions. The presented plots will be denominated "fracture mechanical fatigue curves" in the following. Each point in Fig. 4.25 and Fig. 4.26 is a single measurement. Since the current fracture mechanical test program took already several months no repeated measurements could be performed. Additionally, according to (ISO 18489) single measurements at four different load levels are sufficient for material ranking. Although these statement was postulated for cracked round bar specimens it can also be used for the present work since the POM CT-specimens broke brittle with no evidence of significant plastic deformation ahead of the crack tip.

The lines implemented in the fracture mechanical fatigue curves are logarithmic trend lines. They are rather intended to support the qualitative ranking than to represent quantitative trends.

Fig. 4.25: Fracture mechanical fatigue curves of Delrin

When looking at the fracture mechanical fatigue curves the ones of the CM samples are discussed first. They are a little bit steeper than the IM curves and in case of Tenac the curve is also shifted to higher cycle numbers. The latter definitely means an improved fracture mechanical behavior. Thus Tenac CM specimens performed a little bit better than the corresponding IM specimens while there was no significant difference between CM and IM specimens for Delrin. The vertical shift of the Tenac CM measurement points is an experimental effect (too high load in relation to the specimen thickness). The thickness of the CM plates was only about 80 % of the thickness of the IM plates and so were the loads used. However, the thickness of the CM plates decreased over time (shrinkage) and thus the initially defined load level caused a ΔK which was slightly higher than that of the corresponding IM plates. It has to be emphasized that the K-factor values plotted in Fig. 4.25 and Fig. 4.26 were calculated using the correct specimen dimensions.

Fig. 4.26: Fracture mechanical fatigue curves of Tenac

Concerning the IM plates the specimens which were rotated by 90° (Delrin_IM_90°C-MT_Pos1-90°rot and Tenac_IM_90°C-MT_Pos1-90°rot) performed worse than the average. It has to be mentioned that for the specimen Tenac_IM_90°C-MT_Pos1-90°rot the test with the highest load level (F_{max}=600 N) lead to spontaneous failure and therefore this measurement point is not plotted in the corresponding fracture mechanical fatigue curve (Fig. 4.26). Both, Delrin_IM_90°C-MT_Pos1-90°rot and Tenac_IM_90°C-MT_Pos1-90°rot seem to have a significant drop in the cycles to failure with increasing load level. In comparison, for both materials the curves of the not rotated specimens at the same sample

positions indicate a better mechanical behavior. Hence, it is speculated that the fracture mechanical properties of the IM plates are slightly dependent on the loading direction with regard to the filling direction. Of course it has to be kept in mind that the number of samples which support this impression is low and repeated tests are required for a final conclusion.

All the other fracture mechanical fatigue curves of the IM specimens show a slight tendency to better fracture mechanical behavior from low to high mold temperatures. For Tenac it can be seen quite well. For Delrin the measured points are very close to each other.

Generally, looking at the fracture mechanical fatigue curves of both materials it can be seen that the processing influence on Delrin is smaller than on Tenac. In Fig. 4.27 representative curves of both resins and both processing types used are plotted. The diagram shows that Delrin generally has a slightly better fracture mechanical behavior. Directly compared to the Tenac curves it is even more obvious that the change in the processing conditions had only little influence on the fracture mechanical performance of Delrin. The position of the Tenac_IM_90°-MT_Pos_1 curve shows that Tenac is more sensitive to mold temperature and cooling time.

Fig. 4.27 Comparison of the fracture mechanical fatigue performance of both POM resins (representative curves)

4.3 Correlations between morphology and fracture mechanics

The CM plates showed an influence of the processing conditions on morphology and fracture mechanical properties. Compared to the IM plates the CM specimens of both POM resins

had a degree of crystallinity equal or higher in all tests performed. Their performance in the fatigue fracture tests was better (Tenac) or at least similar (Delrin) to that of the IM specimens and in the PLM pictures they showed a rather homogenous structure. Due to the nucleating agent the spherulites of Delrin were distributed very regularly and because of their great number they were too small to be identified by PLM. A very homogenous structure is less susceptible for defects which could weaken the material. The great number of spherulites and the relatively high molecular weight of Delrin lead to the assumption that the CM plates of Delrin have a high density of TM and entanglements which increases the material's crack resistance. With the 3-component model an increased amount of ECC was detected in the SAXS measurements. These crystal lamellae additionally stabilize the material. However, the results from the SAXS analysis methods should generally be treated with some caution. The methods were not very adequate and some further research work needs to be done in this area.

The performance of Tenac CM in the fatigue fracture tests is comparable to that of the Delrin CM plates. Nevertheless, some morphological differences were found for this variant. Firstly, the slightly lower molecular weight has to be mentioned. As mentioned in chapter 2.2 a higher molecular weight leads to more TM and entanglements and hence, to a better mechanical behavior. Looking at the degree of crystallinity of the various measurements it can be seen that the values of Tenac CM plates were all about 1-3 % lower than for the Delrin CM plates. Of course these differences were very small and their significance is at least partially questionable. What is interesting is that in the PLM the size of the spherulites in Tenac CM plates was much bigger than in Delrin. Additionally, a skin layer was observed for the Tenac plates which Delrin CM plates did not have. Thus from the PLM images alone one could expect that the materials used were widely differing whereas all other results suggest that they were very similar. This leads to the assumption that the influence of the spherulite size is not very significant.

The fracture mechanical fatigue curves of the Delrin IM specimens (except Delrin_IM_90°C-MT_Pos1_90°rot) are very close to each other. Only a slight trend to better mechanical behavior from low to high mold temperatures can be seen. This trend is also reflected in the PLM images. They show that the structure of Delrin becomes more homogenous at higher mold temperatures. The analyses of the degree of crystallinity also followed that trend except for WAXD. For an unknown reason the (100) diffraction peak of the samples analyzed using WAXD increased from 60°C to 90°C mold temperature and then decreased again from 90°C to 110°C. That did not correlate with any of the other findings. However,

the difference in the absolute values of crystallinity was very small (about 1 %) and hence, can also be an ordinary scattering effect.

Tenac_IM (except Tenac_IM_90°C-MT_Pos1_90°rot) showed the same effects as Delrin_IM: The higher the mold temperature the better the fracture mechanical performance, the more homogenous the structure in the PLM images and the higher the degree of crystallinity, except for WAXD where a small peak at 90°C mold temperature was observed. For details regarding the latter please refer to the previous paragraph. A specialty for Tenac IM plates was the layer structure observed in PLM which contained also layers with a very coarse spherulitic substructure. The way the size of the spherulites was distributed (from outside towards the middle of the plates: fine – coarse – fine) is contradicting the conventional expectations for the spherulitic structure in injection molded components. For a more detailed correlation between morphology and fracture mechanical properties the layer substructure should be examined.

The fracture mechanical tests of the 90° rotated specimens of both materials showed a slight drop in the performance. This is interpreted as an effect of orientations. Unfortunately, none of the morphological characterization methods gave any useful information about orientations. The SAXS method which was intended for this parameter suffered from deficiencies. These deficiencies should be identified and eliminated before future investigations. Additionally, from the X-ray point of view further tests using thin layers as samples are suggested. It is expected that the separation in thin layers can give information regarding orientations and their distribution over the specimen thickness. PLM images of samples cut off in different angles with regard to the filling direction should also be taken into account for future studies.

For a more detailed correlation between morphology and fracture mechanical properties future research with additional methods will be necessary. While some of these methods were discussed above others were not especially mentioned. Useful methods can be FTIR, different sample preparation (slicing of the plates) and alternative analysis methods for the SAXS profiles.

5   SUMMARY, CONCLUSIONS & OUTLOOK

POM is an engineering thermoplastic which is usually used in structural parts. In previous studies it was observed that its properties can be strongly influenced by the processing conditions. Aim of this thesis was to find a correlation between processing, morphology and fracture mechanical properties for two different POM resins. For that purpose plates were produced using two different processing types: compression molding and injection molding (with three different mold temperatures). The morphological states of the plates were characterized using X-ray scattering (SAXS) and diffraction (WAXD), polarized light microscopy (PLM) and differential scanning calorimetry (DSC). The SAXS data were analyzed using 1D correlation and a 3-component model obtained from literature. Additionally, for both methods the basic characteristics and the application limits were tested. The fracture mechanical properties of the plates were tested by means of fatigue fracture tests.

The degree of crystallinity was very similar for both materials. The crystallinity of Tenac was constantly slightly lower than that of Delrin. The highest crystallinity was found for the CM specimens. The IM specimens showed an increase in crystallinity for increasing mold temperatures. Generally speaking, these trends were found in all morphological tests (SAXS, WAXD and DSC) but the absolute changes were small. However, these trends were also found for the fracture mechanical fatigue curves. The best fracture mechanical behavior was found for the CM specimens. The fracture mechanical performance of the IM specimens showed an increase with an increase of the mold temperature. Specimens which were cut off the plates with a rotation of 90° with regards to the filling direction showed a small decrease in the fracture mechanical performance. Unfortunately, no orientations of the material were found in any of the morphological tests. Hence, these findings cannot be brought in correlation with the morphology. The PLM images showed great differences between the two materials. Delrin had very small spherulites whereas Tenac had spherulites up to a size of 0.22 mm. The CM plates had a rather homogenous structure. The IM ones had a distinct layer structure which changed with the mold temperature. For Delrin it is not clear yet what the difference between the layers and their origin is. Thus some further research is necessary in this area. Tenac had distinct spherulites with a rather unexpected size distribution.

By repeating some tests but with an alternative sample preparation, e.g. testing thin layers of the materials it is expected to learn more about the morphological substructure of the

materials used. It is also expected that orientations can be detected in that way which would give further insight into the correlation between morphology and fracture mechanical behavior. In the future it should also be considered to use harsher processing parameters in order to increase the differences between the processed variants and to approach to more technical processing conditions.

The two methods used for the analysis of the SAXS data (1D correlation the 3-component model obtained from the literature) lead to results with similar trends in the degree of crystallinity. However, when taking a closer look at the methods they had distinct shortcomings. The basic structure model on which 1D correlation is based is definitely too simple for POM and the profile extrapolation required for the analysis strongly influenced the results. Hence, the way 1D correlation was performed in this work is not recommendable for future research. The 3-component model was promising at the beginning because of the more detailed structure model it is based on. However, when applied for the analysis the results obtained by curve fitting were not satisfying: exact peak positions and shapes were hardly found. Instead of using models like these from the current point of view it would be more promising to use simpler analysis techniques based on the evaluation of areas and positions of the detected peaks.

WAXD was quite easy to handle and it provided reproducible results. The variation in the results of the differently processed specimens was very small (3-4 %) but the standard deviation for each series was also less than 1 %. Hence, the trends in the results can be taken serious. One drawback of this method is the sample size. If the measurement position is too close to an edge shadows of the edge will distort the detected pattern. This drawback could probably be eliminated by adapting the testing setup, e.g. by using metal shields.

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