TAMPERE UNIVERSITY OF TECHNOLOGY

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# EXTRUDER DIE COATINGS IN POLYMER PROCESSING

Master of Science Thesis

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# ABSTRACT

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Extruder die coatings were studied in the extrusion of modified polyethylene (PE-mod). When PE-mod is extruded at elevated temperatures, it will change into a high-viscosity polymer melt causing high pressure inside the extruder die. The temperature is elevated to activate a cross-linking reaction to endow the end product with favoured properties. However, the increased pressure renders difficulties in the extrusion process reducing production rate and increasing power consumption. For the efficient extrusion of PE-mod, a lubricant, non-sticking, and wear resistant coating is needed.

Pressure drop across the extruder die can be decreased by increasing wall slipping. Certain molten polymers exhibit wall slip behaviour along the extruder die surface under sufficient shear stress. Low surface energy coatings, namely fluoropolymers, can substantially enhance slipping but their propensity to wear causes problems. By studying factors inducing wall slip, different coatings and surface treatments were chosen for comparative testing.

Tests were done using a cone extruder with a custom fabricated annular extruder die. Pressure drop and drag force exerted on the torpedo of the die by flowing polymer melt were measured. Altogether six coatings were tested and a two-day continuous extrusion experiment was conducted for a fluoropolymer coating to gain better understanding of the wear characteristics. In addition to pressure and force measurements, post-extrusion analyses for the fluoropolymer coating were made using scanning electron microscopy (SEM), optical profiling, infrared spectroscopy (IR) and differential scanning calorimetry (DSC).

Fluoropolymer coatings were shown to exhibit the strongest wall slipping behaviour by gaining the lowest pressure drops and drag forces over the extruder die surface at the same throughput rate. Wear characterization revealed intriguing result: the slipping behaviour of fluoropolymer coating is impaired by small fractions of PE-mod sticking on the surface of the coating. Furthermore, several improvements were suggested in order to perfect the measurement facilities.

# TIIVISTELMÄ

TAMPEREEN TEKNILLINEN YLIOPISTO
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**PÖYRY, JUHA-PEKKA**: Ekstruusiosuuttimien pinnoitteet polymeerien prosessoinnissa
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Polyeteenistä valmistettujen lopputuotteiden useita ominaisuuksia voidaan parantaa huomattavasti ristisilloittamalla. Prosessoinnissa ristisilloitus aiheuttaa sulaviskositeetin voimakkaan kasvun. Viskositeetin kasvu nostaa sulan painetta ekstruusiosuuttimessa, mikä puolestaan sekä hidastaa tuotantonopeuksia että kasvattaa energiankulutusta. Pinnoittamalla ekstruusiosuutin sulan liukumista edistävällä ja kulutuskestävällä pinnoitteella saadaan ekstruusion painehäviötä laskettua merkittävästi. Painehäviön pieneneminen johtuu wall slip -ilmiöstä, joka kertoo sulan liukumisesta rajapinnoilla. Tietyillä polymeerisulilla ilmenee riittävän suurien leikkausjännitysten toteutuessa wall slip -ilmiö. Voimakas sulan liukuminen on ominaista matalan pintaenergian pinnoitteille, kuten fluoripolymeereille. Niiden huono kulutuskestävyys kuitenkin vaikeuttaa käytäntöön soveltamista.

Tämän työn tarkoituksena oli tutkia suuttimen erilaisten pinnoitemateriaalien vaikutusta modifioidun polyeteenin (PE-mod) prosessointiin. Työssä testattavien kuuden suutinpinnoitteen valitseminen ja rajaus perustuivat pinnoitteita ja wall slip -ilmiötä käsittelevään kirjallisuusselvitykseen. Pinnoitemateriaalit testattiin tekemällä koejaot kartioekstruuderilla, johon oli liitettynä testejä varten valmistettu putkisuutin. Testeissä mitattiin painehäviötä ja putkisuuttimeen kohdistuvaa virtaavan sulan vetovoimaa. Kuudelle testattavalle pinnoitteelle tehtiin voima- ja painehäviömittaukset. Lisäksi fluoripolymeeripohjaiselle pinnoitteelle tehtiin kahden päivän yhtäjaksoinen ekstruusiokoeajo, jonka tarkoituksena oli tutkia pinnoitteen kulumista PE-mod:n ekstruusiossa. Testin jälkeen pinnoitteen kulumista analysoitiin pyyhkäisyelektronimikroskopian (SEM), optisen profiloinnin, infrapunaspektroskopian (FTIR) ja termisen analyysin (DSC) avulla.

Fluoripolymeeripohjaiset pinnoitteet osoittautuivat parhaiten soveltuviksi PE-mod:n ekstruusioon. Näille pinnoitteille mitattiin pienimmät painehäviöt ja vetovoimat vertailtaessa pinnoitteita samalla tilavuusvirtauksella. Kulumisen karakterisoinnissa fluoripolymeeripinnoitteen huomattiin vähitellen keräävän pinnalleen ohuen polyeteenikerroksen, joka aiheuttaa pinnoitteen toiminnallisuuden heikkenemisen. Useita ehdotuksia esitettiin mittauslaitteiston parantamiseksi jatkotutkimuksia silmällä pitäen.

# PREFACE

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Tampere, December 23rd, 2011

Juha-Pekka Pöyry

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# ABBREVIATIONS

| | |
|---|---|
| $\Delta p$ | Pressure drop |
| $\eta$ | Shear viscosity |
| $\eta_0$ | Zero shear viscosity |
| $\tau_w$ | Wall shear stress |
| $R_a$ | Average surface roughness |
| $R_t$ | Maximum roughness height |
| $R_z$ | Ten-point mean roughness |
| $v_s$ | Slip velocity |

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| ATR | Attenuated total reflectance |
| BN | Boron nitride |
| DCP | Dicumyl peroxide |
| DSC | Differential scanning calorimetry |
| EN | Electroless nickel |
| EN BN | Electroless nickel plating with boron nitride |
| FEP | Fluorinated ethylene propylene |
| FP | Fluoropolymer |
| FTIR | Fourier transform infrared spectroscopy |
| GMF | Gross melt fracture |
| h-BN | Hexagonal boron nitride |
| PE-HD | High density polyethylene |
| HFP | Hexafluoropropylene |
| IR | Infrared |
| PE-LD | Low density polyethylene |
| PE-LLD | Linear low density polyethylene |
| LVOF | Low velocity oxy-fuel spraying technique |
| MMD | Molecular mass distribution |
| NMR | Nuclear magnetic resonance |
| PE | Polyethylene |
| PEEK | Polyetheretherketone |
| PE-mod | Modified polyethylene |
| PFA | Perfluoroalkoxy polymer |
| PP | Polypropylene |
| PPA | Polymer processing additive |
| PTFE | Polytetrafluoroethylene |
| SEM | Scanning electron microscopy |
| $VF_2$ | Vinylidene fluoride |
| XPS | X-ray photoelectron spectroscopy |

# 1 INTRODUCTION

Polyethylene is a common plastic from which pipes, profiles, and sheets are manufactured by a method called extrusion. There are thousands of different polyethylene grades. Typical properties of polyethylene include good mechanical strength, chemical resistance, low price, and ease of manufacturing. Mechanical and high-temperature properties are improved when the molecular structure of polyethylene is modified. Three-dimensional networks of strong bonds between separate molecules are formed. However, the production rate of this modified polyethylene (PE-mod) is decreased when the structure is modified because it no longer flows as freely. The performance of extrusion process can be substantially enhanced by applying a lubricant coating or surface treatment on the die wall.

The primary objective of this Thesis is to study extruder die coatings suitable for the extrusion of modified polyethylene. Measurements are done using a cone extruder with a custom fabricated extruder die. When modified polyethylene is extruded, it will cross-link because of the thermal agitation induced by high temperature in the extruder die. Cross-linking transforms PE-mod into very viscous material causing high pressure drop across the die. The pressure can be measured with the custom-made measurement die. Decreasing pressure drop across the die tells how strongly the molten polymer slips along the die wall. This property is affected by the coating of the die. In addition, the drag force imposed to the die is simultaneously measured. Basically, these two measurable values are in direct relationship which makes the tests more reliable.

Selected coatings and surface treatments are tested to evaluate their usability in the extrusion of PE-mod. Coatings consisting of two fluoropolymers, hard chrome plating with fluoropolymer, metal oxide, boron nitride, and electroless nickel with boron nitride were chosen. The comparison between the coatings is based on the pressure drop and drag force data. Furthermore, a coating with desirable properties is tested in a two-day extrusion experiment to assess the wear of coating. In-depth analysis is done using spectroscopy, microscopy, and thermal analysis in addition to pressure drop and drag force measurements. Indeed, the other primary objective of the Thesis is to find out the wear mechanism and gain better understanding of the wear in the extrusion of PE-mod.

Background chapter will provide an overview of the salient concepts in the rheology of extrusion. Rheological introduction is provided to be able to discuss phenomena taking place inside the extruder die. Extrusion of PE-mod is affected by the phenomenon called wall slip. It is the most recognized explanation for decreasing pressure drops across the extruder die. Review of coatings and surface treatments in the polymer processing is presented in the end of the background chapter to provide a basis for choosing promising coatings to the tests. PE-mod was chosen as an extrusion material owing to its heavy wearing properties and lack of suitable wear resistant coating. Without any coating, for example against steel, PE-mod adheres on the surface of die. The cone extruder was used in the study because it enables the measurement of drag force inside the die. A brief introduction to the analysis methods in the wear test is described in Chapter 3. Results and discussion are found in Chapter 4. Finally, concluding remarks and recommendations for future are given in Chapter 5 and 6.

# 2 BACKGROUND

The rapid development of the polymer processing techniques in the second half of the twentieth century has challenged scientists and engineers to gain better understanding of the melt behaviour of polymers. The understanding of viscoelasticity is the backbone in many rheological phenomena that occur in extrusion. Anomalous flow features, like flow instabilities and die swell are attributed to the viscoelastic nature of polymer melt. These phenomena reduce production efficiency and may prove costly. Wall slip is now the most accepted explanation for the flow instabilities. A few theories have been postulated to explain the wall slip and they are discussed in Chapter 2.2. Wall slip is studied closely here because it is the phenomenon that explains decreased die pressures in the extrusion process. Extruder die coatings are sometimes vital for proper performance. This is the case in the extrusion of modified polyethylene. Various coatings and surface treatments have been tested but a long-lasting and slip-inducing option is still to be found. Potential choices for extruder die coatings are presented on Chapter 2.4. (Koopmans et al. 2011)

## 2.1 Basics of Rheology

Rheology is the science of deformation and flow of matter. Rheology is of great importance and interest in plastics fabrication processes because all thermoplastic polymers must flow during the manufacturing process. It is the molecular structure of polymers that poses challenges to their successful processing. Understanding the phenomena taking place in molecular level helps one to comprehend the melt behaviour of polymers. Basic concepts of viscoelasticity, viscosity, viscometric flow, and the role of rheology in extrusion are discussed here. (Chanda & Roy 2006)

### 2.1.1 Viscoelasticity

For an ideal elastic material, that is Hookean, the stress is directly proportional to the deformation. The elastic energy causing deformation is stored in the substance and the deformation is recoverable. On the other hand, for an ideal viscous liquid, that is Newtonian, the shear stress is directly proportional to the rate of deformation. In this case the energy dissipates and the deformation follows the stress with delay. Polymer melts are viscoelastic liquids because they have viscous and elastic properties. The reason for viscoelastic nature of polymer melts lies within the molecular structure. (Chanda & Roy 2006; Aho 2011)

Polymers consist of molecules which are formed by a group of atoms which have strong bonds among themselves but relatively weak bonds to adjacent molecules. These molecules are also called macromolecules because they contain thousands of millions of atoms. (Chanda & Roy 2006) Molecules are entangled with each other and form many flexible, reversible joints. (Aho 2011)

At macromolecular level the random structure of polymer aligns in the direction of the applied force. Under a continuous force the polymer chains will begin to move and flow. This chain motion and flow (deformation) becomes easier, requiring less force when heat is applied to the process. (Hylton 2004) The chain deformation can happen in three ways. The first mechanism is the stretching and bending of the bonds of the atoms within the polymer molecule. This type of deformation is elastic as the deformation recovers to its original position without any delay. The second type of deformation is uncoiling and straightening of the entangled molecule chains. The nature of this type of deformation is also elastic but recovering is time-dependent. The third mode of deformation happens as the polymer chains slip and flow with respect to each other. The deformation happening this way is permanent, or viscous, and it does not recover to its original position. (Hylton 2004)

All the deformation mechanisms occur simultaneously and that is why polymer melts exhibit both viscous and elastic properties. Therefore, this dual nature is referred to as viscoelastic behaviour. It is obvious that factors like polymer structure, temperature, and time have a great effect on which property predominates, viscous or elastic. (Hylton 2004; Chanda & Ray 2005)

### 2.1.2 Viscosity

In polymer science, viscosity is a material property that is regarded as a measure of resistance to flow. Viscosity depends on flow conditions and polymer composition. Flow conditions like shear rate, temperature and pressure have a significant impact on how polymer behaves. Chain structure, molecular mass and molecular mass distribution are important properties that determine viscosity of a given polymer. (Dealy & Wissbrun 1995)

The simplest flow behaviour is represented by a linear relationship between deformation rate and stress. Thereby, a plot of shear stress and shear rate is linear and the slope is the viscosity of a fluid. A material that behaves in this way is called a Newtonian fluid. Water is a perfect example of this kind of fluid. In addition, the Newtonian fluid behaviour is true for low molecular mass polymers and for most high molecular mass polymers at deformation rates close to zero. Newtonian fluid behaviour manifest itself in the viscosity curve as a linear plateau at low shear rates, as shown in Fig. 2.1. It is also known as a zero shear viscosity ($\eta_0$). (Hylton 2004; Chanda & Roy 2006)

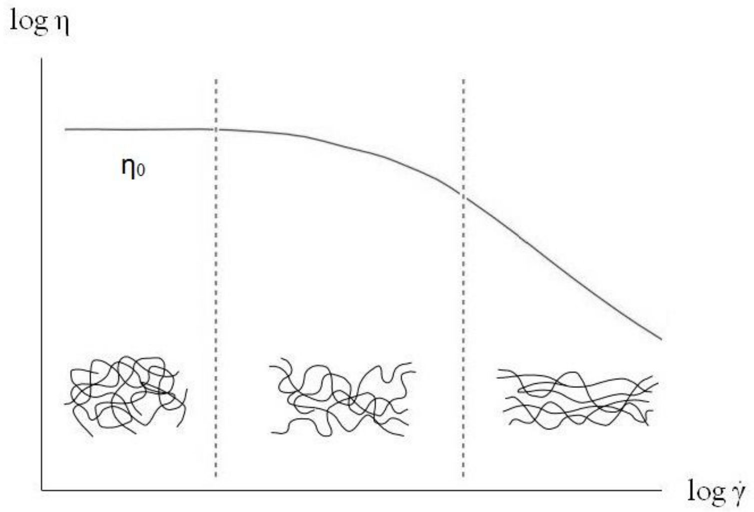


***Figure 2.1.*** *A typical shear viscosity curve plotted against shear rate with a graphic illustration of polymer chains at different shear rates.*

The viscoelastic behaviour of polymer melt in very small or very slow deformations can be described by the theory of linear viscoelasticity (LVE). In the theory of LVE, the viscosity is independent of shear rate. This holds true if the molecules have enough time to relax through Brownian motions and the polymer structure remains unaffected. Brownian motion means that the long and flexible polymer molecules perpetually change their position and configuration by thermal agitation. It is currently understood that Brownian motion is inhibited by the closeness of surrounding molecules, not due to entanglements. At high temperatures the Brownian motion increases the free volume around molecule chains resulting in easier flowing. The opposite happens at temperatures well below glass transition temperature. (Ferry 1980; Dealy & Larson 2006) As the LVE theory is applicable for very small or slow deformations it can be utilized in the characterization of polymers and predicting polymer behaviour by determining the relaxation spectrum. (Hatzikiriakos 2005) The linear viscoelastic behaviour has been modelled with the aid of mechanical spring-dashpot analogies where the dashpot describes the viscous response and the spring the elastic one. (Aho 2011)

However, in most cases, practical deformation rates are often high enough to reach the non-linear region. Also, a polymer of high molecular mass usually exhibits non-Newtonian behaviour. This is because of the entanglements of molecule chains reorganize and orientate along the flow and the melt structure is destroyed (Aho 2011). At the non-Newtonian region it is not possible to describe the flow behaviour with only one constant because the viscosity depends on deformation rate. Thus, the viscosity is expressed as a function of deformation rate. (Hylton 2004) Typically, the melt viscosity of a polymer decreases with increasing shear rate. This phenomenon is called shear thinning. A viscosity curve of a shear thinning polymer melt is presented in Fig. 2.1.

The decreasing viscosity at increasing shear rates is caused by molecule chain orientation and disentanglement. A simple model to describe the shear thinning behaviour is called a power-law model. Usually the power-law model gives a reasonable estimation for processing purposes but higher precision and more complicated models are need for quantitative predictions. Cross, Bueche and Harding, Carreau, and Yasuda have put forth a number of generalised power-law models that take, for example, a zero shear viscosity into account. (Dealy & Wissbrun 1995)

Even though the polymer melts are considered incompressible fluids in molten state in the most of the models, the pressure nonetheless has a small-scale influence on the viscosity and in some processing techniques (usually not in extrusion) it has to be taken into account. Pressure has inverse effects on the viscosity as temperature: viscosity increases with pressure. Higher pressure reduces free volume in the molecular structure and thus the Brownian motion results in a decreased viscosity. (Aho 2011; Kazatchkov 1994)

### 2.1.3 Viscometric Flows

Different types of flow patterns take place around the extrusion die. In extrusion the polymer melt flows from a larger diameter reservoir to a smaller diameter tube or slit and finally exits to the atmosphere. The die geometry creates regions of extensional flow near the contraction. Sudden change in diameters forms recirculating vortices in the corner of reservoir. This tendency increases with the elasticity of the polymer melt. (Mitsoulis 2005; Aho 2011) These vortices are also called secondary flows. A better understanding of the basic characteristics of both shear and extensional flow of viscoelastic polymer melts is important for further study of flow instabilities. (Malkin 1994)

Viscometric flows can be governed by three material functions; viscosity and two normal stress coefficients. These material functions can be derived from differences between stress sensor components arising from deformation. (Dealy & Wissbrun 1995) Steady simple shear is the simplest possible viscometric flow. It can be generated between two parallel plates, where the other plate is moving rectilinear to another while the other is immovable (Fig. 2.2a). The gap between the plates remains constant with time. The consequential simple shear flow is uniform in which each fluid element undergoes exactly the same deformation. (Dealy & Wissbrun 1995)

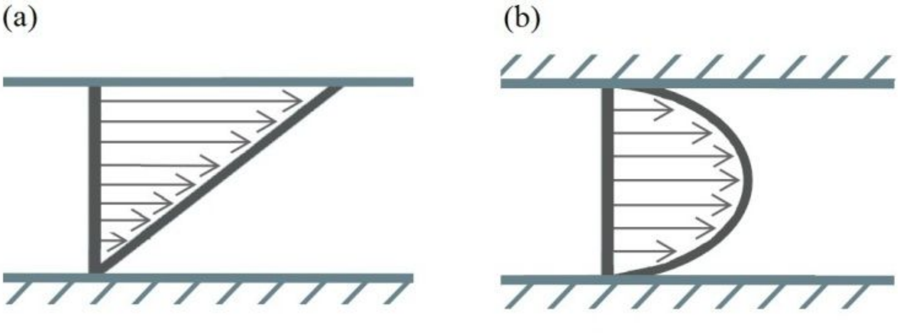


***Figure 2.2.*** *Velocity profiles for a drag flow (a) and pressure driven flow (b).*

The shear flow can be created in two ways; by drag and by pressure. The simplest example of the drag flow is the above-mentioned steady simple shear flow. In pressure driven flow the shearing is generated with the pressure gradient in a closed channel. The pressure driven flow is one of the most common flows in polymer processing because flow channels with static walls are a necessary part in almost all thermoplastic manufacturing processes. The simplest pressure driven flow is tube flow (Fig. 2.2b) that occurs in round cross section channels, e.g. in profile extrusion dies and runner systems inside injection molds. The velocity of the fluid in a tube flow is highest in the centreline of the channel and zero at the wall. And conversely, the shear stress is the highest at the wall and zero in the centreline in fully developed flow. Another pressure driven flow, namely slit flow, occurs in a wide rectangular channel. The edges of the slit channel can be assumed to have negligible effect on flow field when the width to height ratio is more than 10. In a pipe extrusion die with small wall thickness the flow field is close to slit flow because the annular flow channel can be assumed as an unwrapped slit with a high width to height ratio. (Aho 2011; Dealy & Wissbrun 1995)

In extensional flow the material points are stretched along streamlines. This is the case in a flow from larger reservoir to smaller diameter tube where the velocity of material points must accelerate to satisfy mass continuity. Extensional flow is shear-free flow which makes it different from steady and unsteady simple shear flows. Material can be stretched to flow in three ways: uniaxially, biaxially, or in plane. Practically, in the industrial polymer processing the flow is often a mixture of both extensional and shear flows. Extensional flow is especially present in fibre spinning, film blowing, and foaming process. (Dealy 2005; Dealy & Wissbrun 1995)

To date, there is no general model to predict nonlinear viscoelastic melt behaviour but some empirical equations have been proposed. In addition to conservation laws of mass, momentum, and energy, the constitutive equations are needed to simulate the flow behaviour. They connect applied stresses on material to deformation. Furthermore, the constitutive equations can be utilized in finite element method (FEM). (Dealy 2005)

### 2.1.4 Rheology in Extrusion

Extrusion is probably the most important single polymer processing operation. It is a continuous process in which a solid polymer is converted to a melt and forced through a shaping die by the action of a screw. In the extrusion barrel both of the shear flows are present: drag flow is generated by the screw and the pressure flow is a consequence of the die which resist the drag flow. In reality, leakage flow is occurring simultaneously between the screw flight and the barrel which makes the flow analysis more complicated. Flow rate of the polymer melt is affected by polymer viscosity, screw speed, and the geometry of screw and die. (Dealy & Wissbrun 1995)

Understanding rheology in the die region is more crucial to the production quality. Flow instabilities arise in die region and affect the production speed and quality. The knowledge of viscoelasticity and flow behaviour is then needed. However, there is still a shortage of means to accurately simulate the flow as it is so complex. Approximations and simplifying assumptions have to be made. (Rauwendaal 2001) Many difficulties in the polymer extrusion such as die swell, extrusion defects, and melt fracture stem from the viscoelastic behaviour of molten polymers. (Chanda & Roy 2006)

The extrusion process depends on many factors such as material selection, extruder, screw, and die. Any advance on these factors would improve productivity and earn cost savings. Rheology links all these factors together. Understanding it helps one to estimate the process parameters, design the screw and die, and evaluate power requirements. (Rauwendaal 2001)

## 2.2 Wall Slip in Die Flows

The no-slip boundary condition is a central concept in fluid mechanics. (Denn 2001) It states that the relative velocity of the fluid remains zero at the fixed wall. So the viscous fluid adheres to the wall and moves only if the wall moves. However, this is not always the case for polymer melts. (Dealy & Wissbrun 1995) Wall slip of polymer melts was first proposed by de Gennes who theorized that polymer melts should always slip at any shear rate when flowing over a smooth non-adsorbing solid surface. (Tchesnokov 2005) Slipping behaviour on wall is described as a value of slip velocity, $v_s$ (Fig. 2.3). It is now recognised that at sufficient strain rates or stress levels the polymer melt slips near or at the wall. In other words, the wall slip phenomenon violates the basic concept of fluid mechanics that states the melt velocity is zero at the fixed wall. (Dealy & Wissbrun 1995) Wall slip phenomenon has been verified with a variety of direct and indirect methods like particle tracers, laser Doppler velocimetry, Mooney analysis, and gap-dependent measurements. The most common visible implications of wall slip in polymer extrusion processes are irregularities like sharkskin, stick-slip, and gross melt fracture. On the other hand, if the wall slipping is sufficiently strong, it decreases the die pressure and more efficient production is achieved. (Münstedt et al. 2000; Archer 2005; Dubrocq-Baritaud et al. 2011b)

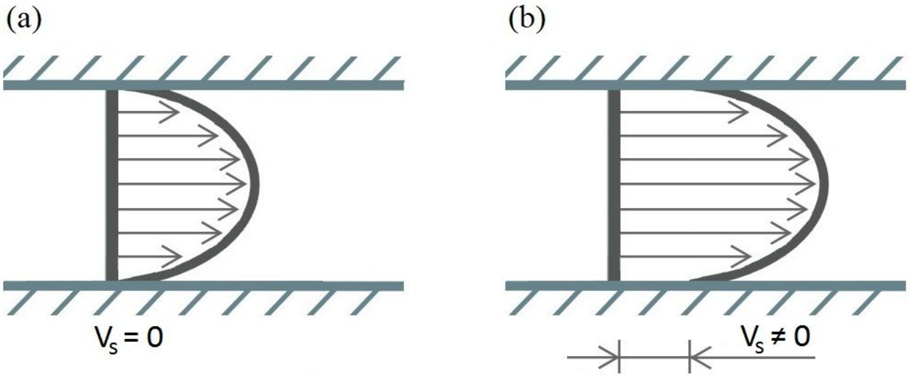


***Figure 2.3.*** *Schematic presentation of no-slip (a) and wall slip (b).*

There are four published mechanisms by which a polymeric fluid may slip: (1) by adhesive failure at the polymer-solid interface; (2) by cohesive failure at a polymer-

polymer interface displaced one or more molecular diameters away from the polymer-solid interface. (3) In multiphase materials, the depletion of more viscous material from the interface may also induce slip. (4) In some cases slip can be explained by shear banding or constitutive instabilities but these mechanisms are still poorly understood. Only the first mechanism actually violates the no-slip assumption as it happens in contact with the substrate. This type of slip is termed true slip. In other situations, slip takes place near the substrate in polymer-polymer interface and for this reason it is commonly termed apparent slip. Slips by adhesive and cohesive failure are the most postulated and find abundant experimental support. In reality, both mechanisms occur in parallel. (Archer 2005) Interfacial conditions like the material of die construction, the surface roughness, and the surface energy of die have a strong influence on the wall slip. (Georgiou 2005)

Adhesive failure was a long time the dominant mechanism explaining wall slip on high-energy surfaces (e.g. steel). For adhesive failure to happen in the polymer-wall interface the polymer molecules must detach from the die wall. Macromolecular detachment requires stresses that overcome the work of adhesion. The work of adhesion describes adhesion between two materials in terms of surface energies. (Koopmans et al. 2011) In addition, diffusion processes may have an effect on adhesion failure if a thin layer of coating is applied to the die wall. (Anastasiadis & Hatzikiriakos 1998)

Adhesive failure mechanism has been studied extensively with low surface energy fluoropolymer coatings. Anastasiadis and Hatzikiriakos (1998) found a linear correlation between the critical shear stress for the onset of slip and the work of adhesion for different die surfaces. This finding suggests that under flow the polymer molecules absorbed on the surface stretch and break off the surface. Debate on whether the low-energy surface promotes or reduces the adhesion on the wall still continues. (Barone & Wang 2000)

Cohesive failure mechanism stems from polymer molecule chain disentanglement from the molecule chains that are absorbed at the wall. The flowing polymer melt slips over an attached polymer chain brush. The long, absorbed molecules are attached to the wall in many points forming loops and tails. Generally, every absorbed chain has two mobile tethered chains and motion restricting loops in the between. In the presence of flow the chain loops will eventually be squeezed against the wall by the flowing bulk and do not interact with the bulk as much as tethered chains. The tendency of chain absorption increases with the surface energy of the wall. (Tchesnokov 2005)

Chemical interactions between polymer melt and a die wall may play an unexpected role especially with metal coatings. Oxidation products (e.g. copper oxide on a brass die) can reduce wall slip but their effect is found to be insignificant compared to the effects of surface roughness and surface energy. (Rutgers & Mackley 2001; Halley & Mackay 1994)

Studying the wall slip and flow properties of molten polymers is not straightforward. Exemplary study was performed by Gang et al. in which they tried to measure a friction coefficient between different wall materials and polyolefin melts. The polymer melt was contained between two movable aluminium plugs and back pressure was applied with gas from the bottom of the barrel. A modified capillary rheometer was used to push the plunger down at constant speed. From the experiment data they calculated the coefficient of friction between polymer melt and the barrel wall material. The friction law holds true only if the polymer melt would stay static. It is now well understood that the polymer melt flows and vortices are formed between two moving plugs so that the assumption of friction law is not satisfied. This kind of measurement device could not be used to measure a friction coefficient. (Gang et al. 1995)

### 2.2.1 Surface Roughness

Surface roughness has been studied as a factor affecting wall slip. It has been verified with low viscosity emulsions and gels but results are scarce and in some cases ambiguous with polymer melts. A myriad of studies have been carried out for different die surfaces with various surface roughnesses in the last two decades. Many of them are open to misinterpretations because no accurate explanation of the experimental part is provided. One such effect is surface roughness. For example, in a sliding plate rheometer study, unusual results were argued because one fluoropolymer coating was found to promote slip while another reduced slip. It was later remarked that the difference in application techniques produced fluoropolymer coatings with different surface topography. Slip reducing fluoropolymer coating had a porous surface with pits on the order of 5 µm while the slip promoting surface was dense and smooth. Physical interlocking was hypothesized to be behind the reduced slip of the fluoropolymer coating. (Halley & Mackay 1994)

Larrazabal et al. noticed in slit die measurements that the critical shear stress for the onset of surface instabilities increased with surface roughness (0.1−15 µm) during the extrusion of PE-HD. SEM images were taken from the steel die walls in order to understand the mechanical interactions. The conclusion was that the asperities and craters found on the die wall act as sites where the polymer chains can interlock or anchor. Two hour continuous extrusion experiment was also made to investigate the polymer-wall interface. The die was cleaned from PE-HD before SEM and X-ray spectroscopy. Only element the X-ray detected on the die surface indicated to carbon. In addition, SEM images showed remains of the polymer chains attached to the die wall. It was suggested that the remains on the die indicated to the cohesive failure on the wall. (Larrazabal et al. 2006a)

A research group led by Piau noticed the effect of surface roughness of a PTFE surface in the study in which they investigated extrudate distortions. They slightly rubbed the surface of PTFE with a grade 600 abrasive paper in a direction parallel to the flow channel (Fig. 2.4b) and compared the results with an unrubbed surface. The flow rate for the onset of extrudate distortions of PE-LLD was found to be twice as high for a parallel rubbed PTFE surface. Perpendicularly rubbed PTFE surface (Fig. 2.4a) had a severe effect on the surface quality as shown in Fig. 2.4c. (Piau et al. 1995)

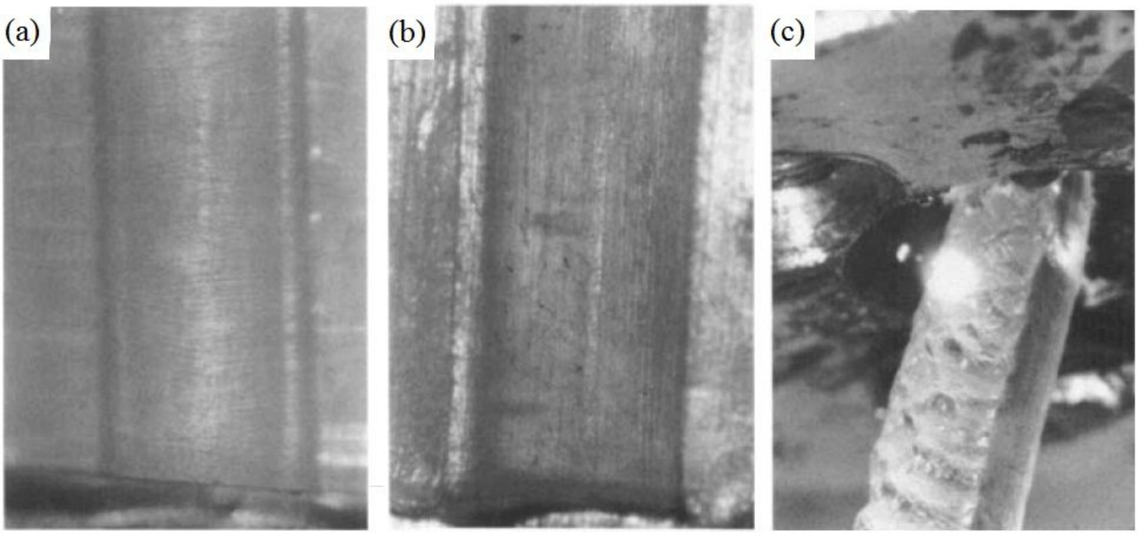


***Figure 2.4.*** *Different PTFE dies were used to compare varied surface roughnesses. Left side of the die wall was rubbed perpendicular to the flow direction (a) and distorted surface was received. Smooth and even surface was attained when right side of the die wall was rubbed parallel to the flow direction (b) (Piau et al. 1995).*

Wang and Drda approached the subject from innovative angle. In addition to a PTFE coated capillary die, they used a similar PTFE coated die which was tapped with screw threads (178 µm deep). Since the valleys of the threads were sufficiently deep, PE melt was trapped in the valleys despite the low surface energy coating. This leads to varying interactions between flowing polymer and stagnant polymer in the threads and evident interactions between polymer melt and coating. The extrusion pressure was greatly increased in a threaded die due to the polymer-polymer interactions for linear PE. In summary, sufficient surface roughness may even prevent the wall slip phenomenon on the low surface energy coatings in which slip normally occurs. (Wang & Drda 1997)

Arda and Mackley compared pressure drops and flow birefringence measurements with three dies with the surface roughness of 0.05, 0.7, and 1.5 µm. Tests were carried out for PE-LLD and PE-HD. They found that the smoother die surface led to reduction in the magnitude of sharkskin. Partial slip was explained to reduce the effect. Pressure drops were significantly higher for PE-HD. (Arda & Mackley 2005) Decreased slip velocities with increasing surface roughness have also been reported by other research groups. (Chen et al. 1993; Mhetar & Archer 1998)

### 2.2.2 Surface Energy

Surface energy is defined as the energy required to create a new surface. Surface energy of a solid surface is most easily estimated from the contact angle of a liquid droplet. The angle is formed by the solid-liquid interface. One has to measure contact angles of two different test liquids for one solid test piece, because the total surface energy for any solid consists of dispersive (nonpolar) and nondispersive (polar) components. Finally, the solid-liquid interfacial tension can be calculated by using Young and Good−Girifalco's equations, for instance. The result is an estimation of interaction between two materials. Relative affinity of two materials has been used to estimate the interaction between polymer melt and die wall. (Rathod & Hatzikiriakos 2004) Comparison of polymer processing additives' relative affinity has also been used to estimate their migration to the die wall (Chapter 2.4.3).

Thesis work by Tchesnokov concerned interactions between flowing polymer melt and a die wall. Numerical simulation was used to find out that the dominant slip mechanism is determined by adhesion energy and melt temperature. For large adhesion energy the dominant mechanism is cohesive while for small adhesion energy the polymer melt may slip on other mechanisms depending on melt temperature. Elevated temperature enhances polymer chain desorption from the wall which according to Tchesnokov leads to both adhesive and cohesive slip. (Tchesnokov 2005)

The strength of interactions between polymer melt and a die wall can be described by defining the work of adhesion. It is a reversible work required to separate a unit area of liquid from a substance. Work of adhesion can be represented by comparing the interfacial surface energy to the surface energies of each of the two materials in the same manner than in contact angle calculations. A widely used equation to solve it from the surface tension and contact angle values is called Young−Dupré. Chen et al. studied different capillary materials and the wall slip velocities for PE-LLD. The surface roughness and chemical structure of capillaries of aluminium, copper, stainless steel, and glass were chosen. They made a predictable observation: the slip velocity decreased with increasing surface roughness. Slip velocity for PE-LLD on glass is interplay of two opposing effects: the smooth surface of glass (slip promoting effect) and the high adhesion of PE-LLD for glass (slip inhibiting effect). The overlapping effect of the surface roughness and adhesion makes it tentative to compare results. (Chen et al. 1993; Anastasiadis & Hatzikiriakos 1998; Larrazabal et al. 2006b)

## 2.3 Flow Instabilities

During the extrusion of polymers different flow instabilities arise that affect the appearance and performance of the extrudate. The most common instabilities are sharkskin, stick–slip, and gross melt fracture. As these phenomena depend on shear rate and shear stress it is convenient to examine them in a flow curve representation (Fig. 2.5). All the polymers do not exhibit the same instabilities nor are the effects of instabilities on flow the same either. The molecular structure (e.g. molecular mass) and the processing conditions (e.g. die coating) affect the way polymer melt flows. (Georgiou 2005)

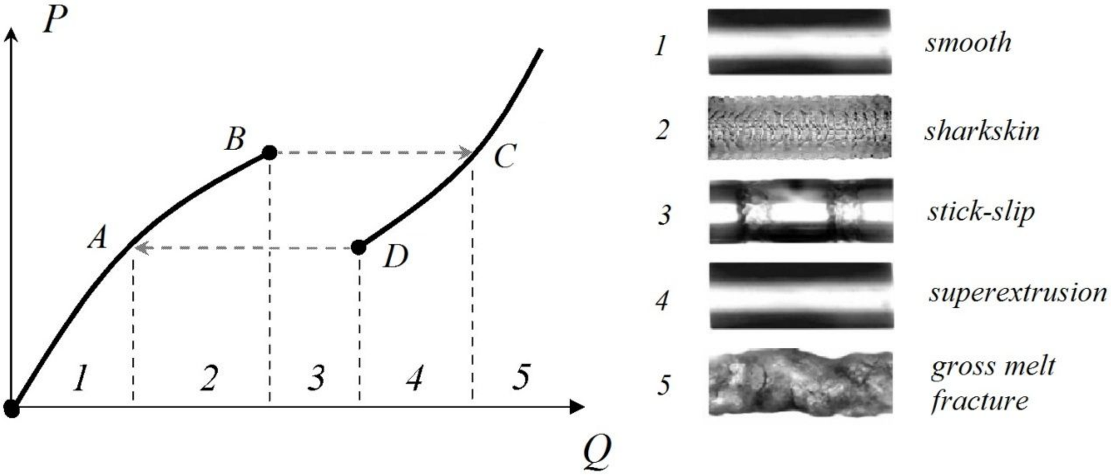


***Figure 2.5.*** *Typical flow curve for a linear polymer illustrating the various regions of instability.*

The ideal smooth surface of the extrudate appears at low shear rate and stress. After the increase in shear rate or stress the first flow instability occurs. Sharkskin effect manifests itself as a uniformly ridged surface. The onset of the phenomenon can be predicted from the flow curve as a change of the slope. Stick–slip flow is characterized by oscillating pressure and spurt flow, and it appears with alternating smooth and distorted surface. Finally, the most rough flow instability called gross melt fracture (GMF) occurs at high shear rates or stress.

Flow instabilities are fascinating from the scientific point of view but can cause a lot of trouble in the industrial production. Flowing polymer melt is affected by various effects such as normal stress and elasticity, strong extensional viscosity, and wall slip. (Hatzikiriakos & Migler 2005) For example, the wall slip effect plays important role in reducing pressure in extrusion dies for better processing capacity. Indeed, it is one focus in this study, and hence, the thorough review of flow instabilities is well-founded.

### 2.3.1 Sharkskin

Undesired irregularity on the surface of the extrudate, known as sharkskin, is a regular ridged distortion perpendicular to the flow. Sharkskin is the first and the most troublesome of flow instability to occur on the extrudate surface as the extrusion throughput increases. At first, the glossy surface turns to matte which means that the amplitude and the wavelength of the distortions are small with respect to the diameter of the extrudate. As the extrusion throughput increases the amplitude and the wavelength increase too and the sharkskin effect is easier to recognize. The surface of the extrudate loses its gloss and changes certain surface properties. Sharkskin is especially very common phenomenon in the extrusion of sufficiently narrow molecular mass polyethylenes. Sharkskin has attracted a lot of academic and industrial attention because it restricts processing capacity and it is the first problem to be solved before other flow instabilities emerge. (Migler 2005)

Sharkskin phenomenon stems from the complex interactions at the polymer–solid interfaces and the viscoelastic nature of polymers. Two reasonable mechanisms have been postulated to explain the phenomenon; the exit stick–slip and rupture hypothesis. The exit stick–slip hypothesis is not to be confused with stick–slip flow instability discussed in the next chapter. The idea of the exit stick–slip hypothesis is based on unstable boundary condition at the die exit. The hypothesis states that the ridges are formed at the die exit where the molten polymer swells more on the stick phase as the built-up elastic energy of polymer melt is released, and less on the slip phase as the flow is more plug-like because of low elastic energy built-up. At certain point the critical stress level exceeds and the slip occurs causing a valley structure on the extrudate surface. A broad range of wall shear stresses (0.1 to 2 MPa) have been found to initiate the sharkskin phenomenon depending on the material in question. In the case of sharkskin the slip occurs only at the exit of the die not on the entire die wall. The elastic energy and the stress start to increase again after the slip occurs causing the die swell to increase at the exit. This cycle of the stick and slip phase at the exit of the die is one hypothesis to explain sharkskin effect. (Migler 2005)

The other hypothesis known as Cogswell model has emphasis on the stretching of the polymer melt near the wall as it exits the die. Sharkskin kinetics by Cogswell model is presented in Fig. 2.6. The stretching causes an extensional stress to exceed a critical value and the surface of molten polymer cracks as the velocity of the melt accelerates (Fig. 2.6 AB). The extensional strain rate of the melt represented by arrow 2 is decreased as the polymer flows now near the wall in the exit area. Subsequently, the fracture grows in size and finally detaches from the die as the extensional strength of the melt exceeds. The detached fracture moves off and the flow in the core continues. (Migler 2005)

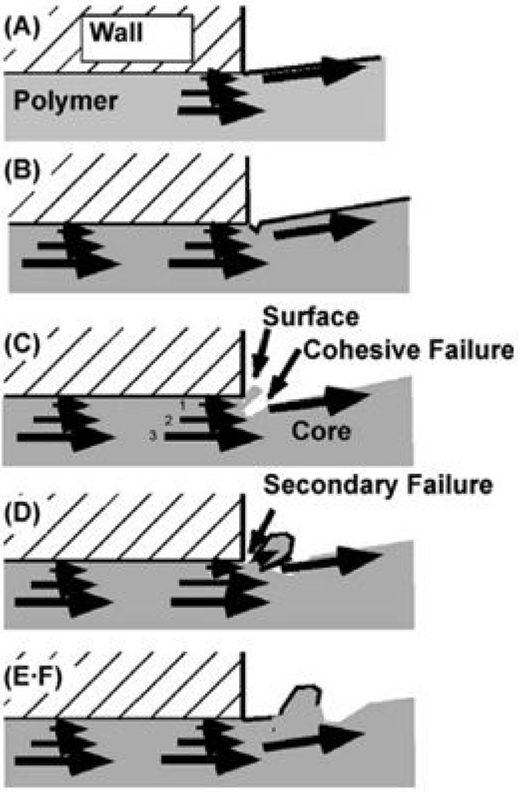


***Figure 2.6.*** *Schematic picture of sharkskin melt fracture model by Cogswell (Migler 2005).*

The Cogswell model provides an explanation for the fact that the extrudate diameter in the valley regions is smaller than the diameter of the die because of the large extensional deformation near the wall (Inn et al. 1998). The exit stick–slip hypothesis has no explanation for this. Also, the connection between the sharkskin effect and narrow molecular mass distribution (MMD) polymer can be explained by Cogswell model. Polymers with narrow MMD are not as elastic as their wide MMD cousins. In a more elastic polymer the extensional stress will take longer to build up and thus may not exceed the critical value for the fracture to occur. (Migler 2005)

The die geometry is decisive in whether the sharkskin occurs in polymer processing, suggested Delgadillo-Velázquez et al. in their recently published study. Capillary, slit, and annular dies have different surface areas compared with volume which passes the die. Based on the Cogswell model, it was argued that the largest surface area of annular die enhances the polymer melt's ability to dissipate energy at the die exit and postpone, or even eliminate, the sharkskin. It was proposed that a critical surface stress condition per surface area must be met before the sharkskin occurs. Experiments were carried out with PE-LLD. (Delgadillo-Velázquez et al. 2008)

Many explanations along with numerical studies of flow conditions (Venet & Vergnes 2000; Rutgers & Mackley 2001) have been postulated to explain the sharkskin. It seems that the exit region initiation of the phenomenon is the only agreement made so far. Comprehensive article by Migler (2005) gives an excellent review of the most popular mechanisms causing sharkskin that have been discussed in the academic field up to date.

### 2.3.2 Stick–Slip

The stick–slip instability is associated with oscillating pressure and flow rate during a constant throughput. The phenomenon occurs at shear rates above the sharkskin effect. Compared with relatively small distortions by sharkskin, the extrudate affected by stick–slip appears to have distinctive and alternating rough and smooth zones. Another difference between sharkskin and stick–slip is that the stick–slip initiates in the die land region whereas sharkskin is known to originate in the die exit region.

Stick–slip pattern is easy to understand from a typical flow curve of linear polymer melt presented in Fig. 2.5. In pressure-driven extrusion the shear rate increases with pressure and follows the left branch of the flow curve until it reaches its end (A). At this point, known as critical shear stress value, the flow rate increases abruptly and jumps to the right branch in the flow curve (B). If the pressure is then decreased, the shear rate decreases until it reaches the end of the right curve (C) and jumps back to the same level of the left curve (D). The result is a hysteresis loop. Consequently, in pressure controlled extrusion the shear rates between A and C are never experienced. This also means that two different shear rates are possible for one shear stress. In flow rate controlled experiment at the shear rates between points A and C, the flow rate and pressure oscillates continuously until shear rate decrease below point A or increase above point C. The oscillations between different shear rates are explained by weak slip (D–A) and strong slip (B–C). The appearance of the extrudate in two separate segments appear to be sharkskinned in the ascending pressure region and gross (or smooth if superextrusion occurs) on the descending pressure region depending on the material in question. (Hatzikiriakos & Dealy 1992)

At macromolecular level, the transitions between the curves can be understood by examining slippage. The weak slip on the left branch of the curve is caused by the adhesive failure of the molecules attached to the solid wall. Greater shear stress (or shear rate) increases the amount of molecules detaching from the solid and thus increasing the slip velocity. The strong slip on the right branch of the curve is associated with cohesive failure. The molecules near to solid wall are disentangled from the bulk and the plug-like slip occurs a few molecules away from the solid wall. Needless to say, the characteristics of the solid wall and the polymer melt have a remarkable effect on the magnitude of the slip. (Georgiou 2005)

Stick–slip under controlled stress was studied by Drda & Wang for a linear PE using capillary rheometer. The violation of no-slip condition was characterized by an extrapolation length b. It was attested that the $b$ was independent of measurement temperature from which they concluded that the slip phase arises from chain disentanglement rather than chain desorption. The measurement temperature would have had an effect if it were a chain desorption induced slip. The stick phase is presented in Fig. 2.7a in which the entanglement between the flowing polymer chains and the absorbed chains occurs. At critical stress value the disentanglement occurs and the interfacial layer, which is exaggeratedly presented in Fig. 2.7b, is separated and flows at the slip velocity of $v_S$. Dots in Fig. 2.7 represent chain entanglements. (Drda & Wang 1995)

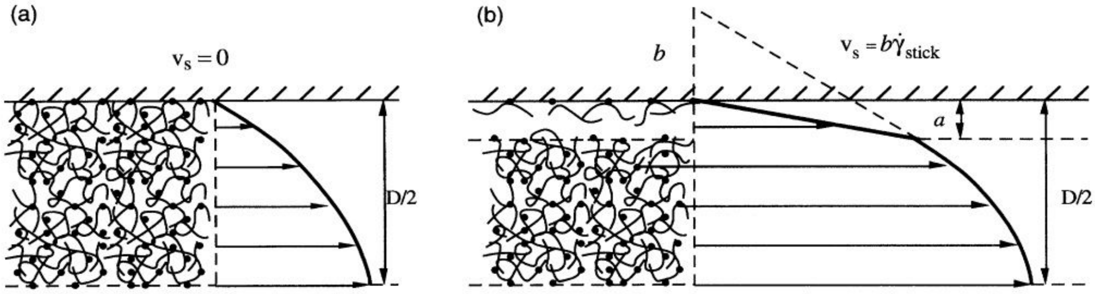


***Figure 2.7.*** *Schematic picture depicting stick (a) and slip (b) phases. (modified from Drda & Wang 1995)*

Two reasonable mechanisms have been suggested for the stick–slip phenomenon. The most popular of them is known as compressibility-slip mechanism. It states that the oscillations in flow rate and pressure are sustained by the compressibility of the melt in a reservoir. In elasticity-slip mechanism, the melt compressibility is replaced by the viscoelastic ability of the polymer melt to enable oscillations in pressure and flow rate. The shortage of this mechanism is its inability to explain larger oscillations. (Georgiou 2005)

### 2.3.3 Gross Melt Fracture

The most severe flow instability can be described as a pronounced chaotic distortion of extrudate. The gross melt fracture (GMF) originates from the flow behaviour at the entrance of the converging die at high flow rates above sharkskin and stick–slip. Piau and coworkers have studied the origin of GMF with capillary experiment using an orifice die. The rough distortions did not disappear even though the die wall was missing which implies that the origin of the phenomenon is not in the die wall. (Dealy & Kim 2005)

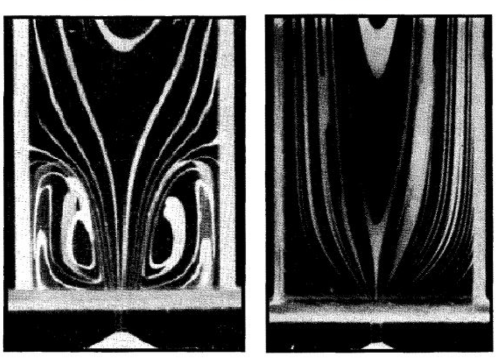


***Figure 2.8.*** *Flow patterns of PE-LD and PE-HD near a capillary contraction (Bagley & Birks 1960).*

The converging die entrance gives rise to vortex flow in the corner of the reservoir. These vortices break the centreline streamline and the circulating melt in the corners join the stream at irregular intervals. The intervals are very brief and the centreline stream quickly re-establishes itself only to break back again. The developing cycle generates the irregular and rough distortion known as gross melt fracture. A classic example of flow behaviours near a die entrance for PE-LD and PE-HD is presented in Fig 2.8. It is good to remember that not all polymers exhibit the same phenomenon. (Mitsoulis 2005)

## 2.4 Extruder Die Coatings

Extrusion dies have to meet a large number of requirements. Basic requirements for die construction include resistance to pressure, temperature and wear with sufficient strength, hardness, and toughness. Ideal die should offer relevant interfacial properties, does not change dimensions during heating, have a good thermal conductivity and resistance to chemical attack. However, these requirements are difficult to achieve with only one construction material and different surface treatments and coatings have become ever more popular practice to improve the die functionality. The most common die material is steel which can be case hardened, fully hardened, nitrided, quenched and tempered depending on the intended purpose. Non-ferrous materials like aluminium, brass, and bronze are rarely used because they lack the hardness and adequate wear properties in most applications of plastics processing. Wear and corrosion resistance can be enhanced by using hard chrome plating, nickel coating, or titanium carbide coating for instance. (Michaeli 2004) The emphasis in this study is mainly related to interfacial properties which determine flow behaviour and, hence, affect throughput and consequent productivity.

There is a great deal of studies comparing different die materials and coatings in which their interfacial properties with polymer melt is thoroughly investigated. A well-known study by Ramamurthy on the influence of die materials concretely demonstrated that the die material plays important role in eliminating flow instabilities such as shark-skin distortion. The experiments were carried out using narrow MMD PE-LLD and PE-HD. It was discovered that the onset of flow instabilities significantly delayed using an α-brass die instead of a then commonly used hard chrome-plated steel die in blow molding. Huge economic benefits could be achieved by brass die because the production rate was increased by 300 % compared with conventional steel die. The observed extrudate irregularities were suggested to be caused by the breakdown of adhesion at the polymer-metal interface. He claimed that promoting adhesion between polymer and die material would eliminate and delay unwanted flow instabilities. (Ramamurthy 1986; Halley & Mackay 1994)

Ramamurthy’s observations were later corroborated by Ghanta and coworkers. However, the mechanism causing the elimination of flow instabilities were contradicted.

It is currently believed that reducing adhesion and promoting slip is the key to decrease flow instabilities. Another remark they made concerned about the oxidative atmosphere in the die. Ghanta et al. used a purging agent and nitrogen atmosphere to prevent the oxidation in the die surface. It was speculated that the nitrogen might reduce oxidative coupling between the polymer and the surface. Exposure to the metallic brass surface could enhance degradation reactions, resulting in a lubricating surface layer of lower molecular mass on which the bulk slides. (Ghanta et al. 1999)

Wu et al. studied the effect of die material on die pressure for metallocene-catalysed PE-LLD. A steel, brass and PTFE die were used. Consistent with previous studies, the steel die had the highest pressures and PTFE die the lowest on the entire shear rate spectrum. At a shear rate of 60 $s^{-1}$ the die pressure was nearly 40 % lower for the PTFE die compared to the steel die due to the very weak adhesion at the wall. The production rate comparisons were in correlation with the die pressure measurements. (Wu et al. 2004)

Like above-mentioned studies clearly demonstrate, the die surface material has an enormous effect on how the polymer extrudes through the die. The die does not only enable the extrusion process but define the extrusion quality. The extrusion process of PE-mod is very demanding in respect of resulting pressure drop across the die affecting the production output. In addition, a high surface quality has to be achieved to meet visual requirements. The standard solution in the PE-mod extrusion is still a fluoropolymer coated steel die. Fluoropolymer and other coatings are introduced in Chapter 2.4.1.

Coating the die is not the only mean to improve the performance of the die. The most widely used modification of the extrusion die wall in polymer processing industry has been the incorporation of fluoropolymers as polymer processing additives. The most common additives have been fluoropolymers and boron nitride. The mechanism, role and some research examples are viewed in Chapter 2.4.2.

### 2.4.1 Die Coatings and Surface Treatments

There are coatings and surface treatments for various purposes. The emphasis in this study is on the coatings and surface treatments that are suitable for PE-mod extrusion. The most important parameters are surface energy, wear resistance, high thermal stability, and coefficient of friction. Friction coefficient is measured between two solid materials and thus the results do not always correlate to the situation in polymer processing where the material interaction takes place between fluid and solid. However, in many cases coefficient of friction can be used to predict lubricity of polymer melts. Due to the slow wear rate of coating, the polymer induced wear measurements are scarce. This is the case especially with metal coatings. Traditionally used coatings and surface treatments as well as recently discovered and promising coatings are introduced below.

### Metal Coatings

The most common metal coatings in polymer extrusion are hard chromium, nickel, and a couple of metal nitrides. Heat treating, nitrating, and hard chromium plating are conventional ways of protecting the surfaces against wear in polymer processing. (Cunha et al. 2002)

Hard chromium plating produces corrosion resistant, wear resistant, and highly polished surfaces, to which polymer molecule chains attach only weakly. Chrome plate is usually used at thicknesses ranging between 15−30 µm. The chromium layer is applied electrolytically and therefore is prone to uneven deposition in edges and corners. Also, the electrolytic process depends on the person making the anode, so the quality can vary from coating to coating. (Michaeli 2004; Hendess 2002) A drawback of hard chromium plating is a formation of micro and macro cracks on the surface (Fig. 2.9). It seems likely that polymer melt will be trapped in the pores and scratches on the surface making the coating perform worse. (Bull & Zhou 2001) One can make use of these micro and macro cracks by packing the openings with fluoropolymer (e.g., PTFE) to produce a lubricious surface. The conditions during plating determine whether small micro-cracks or nearly visible macro-cracks are formed. Cracking occurs during the plating process when internal stress exceeds the tensile strength of the chromium.

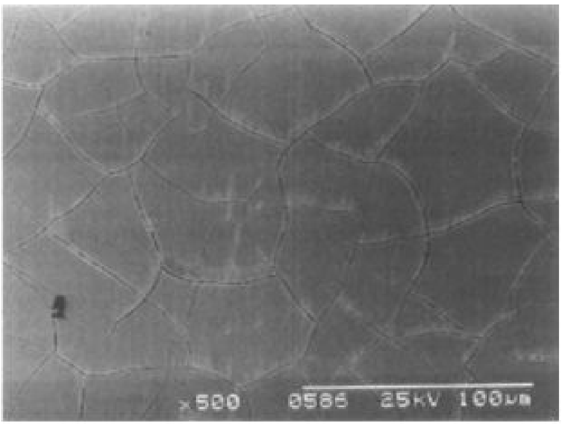


***Figure 2.9.*** *SEM of the hard chromium coating showing the network of micro-cracks (Bull & Zhou 2001).*

Modern nickel plating, namely electroless method, provides an even and pore-free coating because the autocatalytic (electroless) reaction deposits a uniform layer of nickel-phosphorus on a solid without the need of passing an electric current through the solution. Generally electroless nickel (EN) is an alloy of 88−99 % of nickel and the balance usually with phosphorous. The nickel plate is hard, corrosion resistant and has a low coefficient of friction (0.05−0.4). (Hendess 2002) In addition, it is possible to incorporate small particles into EN to form composite coatings. These particles can further forge properties of EN to provide even more hardness, lower friction, and wear resistance. PTFE particles have been widely used but their somewhat poor wear resistance have limited the usage. Harder particles, especially those of ceramics, have recently gained support. Coefficient of friction as low as 0.08 for EN-BN composite has been reported. (Defosse 2009) Nickel-phosphorus coating with a thin film of fluoropolymer on the surface performed very badly in the work by Lahtinen in which trial pipe extrusion runs were performed for PE. Poor performance in the trial runs meant the most die drool formation of the various coatings. (Lahtinen 1997)

The high hardness, good wear, and corrosion resistance make metal nitride coatings popular among tool and machine makers. Gold coloured titanium nitride is the best known of these. Coefficient of friction for these nitrides is in the range of 0.4 to 0.7 depending on the dry sliding parameters. Titanium nitride has been mainly used in metal cutting applications but nowadays nitride coatings, especially those of titanium and chromium, have been used in plastic injection moulding moulds to increase wear resistance under the flow of glass reinforced thermoplastic melt. These coatings have increased the wear resistance compared to heat treated steels. (Cunha et al. 2002)

### Fluoropolymer Coatings

Fluoropolymers have been utilized as a die coating to increase throughput, improve surface quality, and economize production. Fluoropolymer coated die surfaces promote interfacial slip by preventing polymer chains to absorb on the die wall. The use of fluorinated surfaces also eliminate or significantly delay flow instabilities such as sharkskin. There are enormous amount of fluoropolymers used in the academic and technical literature but the focus here is on three commercially available fluoropolymer coatings presented in Fig. 2.10. (Georgiou 2005; Piau et al. 1995; Dhori et al. 1997)

The properties of fluoropolymers stem from the high-strength carbon-fluorine covalent bonds (C−F = 552 kJ/mole) and, of course, the backbone bonds between carbon atoms (C−C = 607 kJ/mole). Uniform and continuous covering of the large fluorine atoms protect carbon-carbon bonds from attacks making it thermally and chemically stable. PTFE has very low surface energy and good thermal stability up to 260 °C. Surface energy of PTFE coating is about 0.02 N/m compared with metallic surfaces' 1 N/m. It is highly crystalline (98 %) and has one of the lowest coefficient of friction against solid, usually reported to be roughly 0.1. The die coatings are usually prepared by spraying or by evaporating the solvent from a polymer solution (Koopmans 2011). The downside of PTFE is its short life as a working coating. One way or another it loses its good frictional properties in the extrusion of PE-mod. One focus of this study is to figure out the mechanism behind it. (McKeen 2006, Chapman 1992)

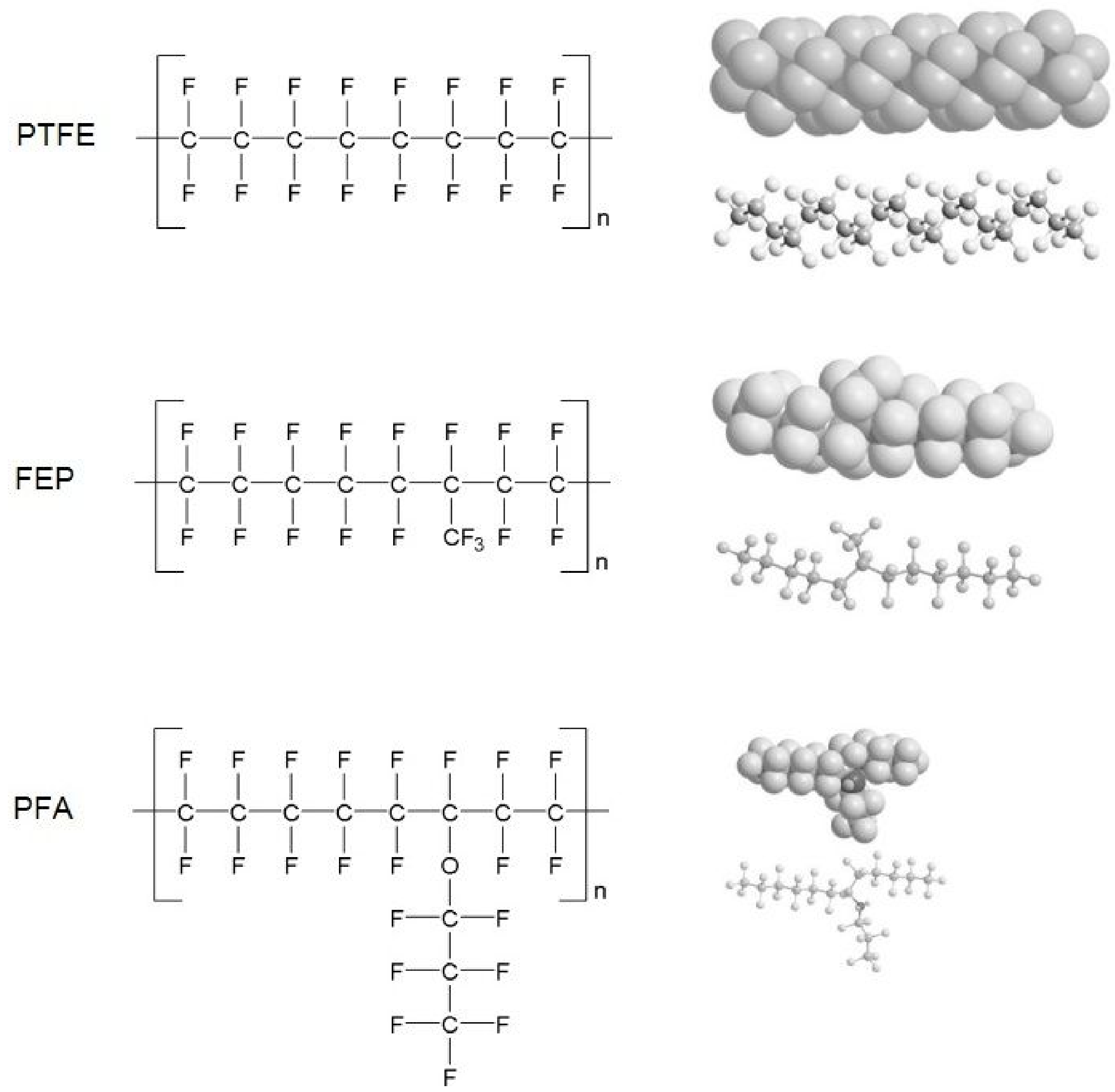


*Figure 2.10. Chemical structures and three-dimensional presentations of the most common fluoropolymers in coating applications (McKeen 2006).*

Piau et al. studied different die walls with a special die for PE-LLD. The machined die (length of 20 mm), into which a PTFE ring (effective length of 1 mm and 5 mm) was possible to mount, was used to investigate the effect of die wall on extrudate distortions. A clear difference in the extrusion rates, in which extrudate distortions appear, was noticed between steel and PTFE surface. A further small improvement was obtained when the slippery surface length was increased from 1 mm to 5 mm because the stresses in the flowing were reduced. It was important finding that the die land has little effect on the surface distortions compared to the exit die region. (Piau et al. 1995)

Capillary rheometer measurements were carried out by Hatzikiriakos and coworkers for PTFE coated slit dies. Their focus was on extrudate distortions which were completely suppressed with the coating. Additionally, a 20 % reduction in applied force was attained and the extrudate swell was decreased. An interesting observation was made when extrusion was continued longer test period (2 h). They noticed a further load reduction that indicates the surface smoothed out providing a better surface for slippage. (Hatzikiriakos et al. 1995)

Fluorinated ethylene propylene (FEP) is formed if one of the fluorine atoms of the monomer of PTFE is replaced with a trifluoromethyl group ($-CF_3$) and it is polymerized with the monomers of PTFE. The trifluoromethyl group containing monomers are usually polymerized with 20 (or more) PTFE monomers. The side group disrupts crystallization which is typically about 70 % for FEP. While the melting temperature decreases (274 °C) compared to PTFE (320–342 °C), most of the important coating properties, like low surface energy and low friction coefficient, are retained. (McKeen 2006)

Perfluoroalkoxy polymer (PFA) is also a useful fluoropolymer in coating applications due to the low coefficient of friction and low reactivity. A side group of perfluoroalkylvinylether ($-O-R_f$, where $R_f$ refer to any number of totally fluorinated carbons) is added to the PTFE backbone at only a couple mole percent. Perfluoropropyl, with three carbon atoms, is a typical side group. The consequent polymer has the same thermal stability of 260 °C and low frictional properties as PTFE. Crystallinity is the lowest of the three fluoropolymers because of the large size of the side group. (McKeen 2006)

#### PEEK Coatings

Polyetheretherketone (PEEK) is a semicrystalline thermoplastic polymer with excellent thermal stability, good wear resistance and tribological properties. Conventionally, PEEK has been used in bearings for its tribological properties and in cable and wire insulation owing to its high thermal stability. The melting temperature of 343 °C and continuous operating temperature of 260 °C guarantee its wide application possibilities. However, it is only recently that its potential as coating material has been investigated. Consequently, the coating techniques have been improving and there are several methods available from thermal spraying to printing and electrophoretic deposition. (Corni et al. 2008)

In a very recent study a composite coating was prepared consisting of PEEK and hexagonal boron nitride (h-BN) particles. PEEK (48 µm) and h-BN (100 nm) particles were mixed together in an ethanol solvent ultrasonic bath under frequency of 50 Hz for 15 min. The composite was then sprayed on a steel plate using a low velocity oxy-fuel (LVOF) spraying technique. Sliding wear tests were performed using a ball-on-disc apparatus. Depositing h-BN up to 10 wt-% increased the wear resistance, surface roughness and hardness compared to lower depositions and pure PEEK. The average friction coefficient was found to decrease close to 0.2 as h-BN content increased. The results revealed that the PEEK composite coating could compete with the properties of PTFE coating. (Thajarak et al. 2011)

Zhang et al. examined PEEK coating applied with flame spraying technique to find out that the coating adherence weakened with annealing (180−300 °C). They concluded that the weak adherence could be related to residual stress produced during the isothermal treatment. The coating was sprayed on a flat aluminium sheet. Surface roughening, like gentle grit-blasting (Palathai et al. 2008), could enhance the adherence by mechanical interlocking. (Zhang et al. 2007)

There is an abundance of studies on the friction and wear properties of PEEK but almost all of them are dry sliding measurements made with pin-on-disc or ball-on-disc apparatuses. The mechanisms of wear and friction in polymer melt−polymer coating interface remain unexplored.

#### Silicone Rubber Coatings

A new coating material in the PE-LLD extrusion was proposed by Kulikov and Hornung. Along with stainless steel, brass, fluoropolymer, and boron nitride coatings they investigated a silicone rubber coating. Surprisingly, rubber coatings delayed the surface defects to at least 10 times higher extrudate velocities compared to PTFE coated dies. They speculated that the flexibility of the rubber surface at micro-molecular level enables attached polymer chains to escape from the voids and pores more easily. In other words, the adhesion is reduced because of the stretching of rubber. Experiments were performed in temperature range of 158−207 °C. (Kulikov & Hornung 2004)

### 2.4.2 Polymer Processing Additives

Polymer processing additives (PPA) are widely used to eliminate flow instabilities and to reduce die pressure in polymer extrusion. In other words, the product quality and processability is enhanced, and power requirements for economical production are reduced. In effect, PPAs are often added to the polymer resin as part of an additive package by resin manufacturers. Typically only a small mass fraction of PPA (approximately up to 0.1 wt-%) is needed. Two-step process is often utilized to guarantee a homogenous dispersion; a so-called master batch is prepared by mixing a dilute blend of PPA (e.g. 10 %) which is easier to mix with the process polymer. Once in process, the PPAs discontinuously coat the die surface with a slippage promoting agent which induces polymer melt to slip. As a result of slippage, the stresses in extrusion are reduced and more efficient production is achieved. There are also disadvantages of PPAs, namely, accurate dosage, additional costs, and possibly harmful interactions with other additives in the polymer. (Kharchenko et al. 2005; Dubrocq-Baritaud et al. 2011b; Achilleos et al. 2002; Migler et al. 2001)

Surface energy calculations have been used to measure PPAs’ ability to suppress flow instabilities. Schematic diagram of relative affinity of PTFE and BN in extrusion is presented in Fig. 2.11. Relative affinity is calculated by comparing the contact angle values of two materials and it describes the level of interaction between them. The diagram clearly depicts why PTFE is so a good die coating. PTFE has very high affinity for the die wall and practically zero affinity for the polymer. Thus, PTFE behaves as an external lubricant by migrating to the die wall and allowing polymer melt to slip over. BN powders have moderate surface energy and are mildly polar. Their relatively high affinity for the PE-LLD provides effective lubrication within the polymer melt by removing friction between the polymer chains. (Rathod & Hatzikiriakos 2004)

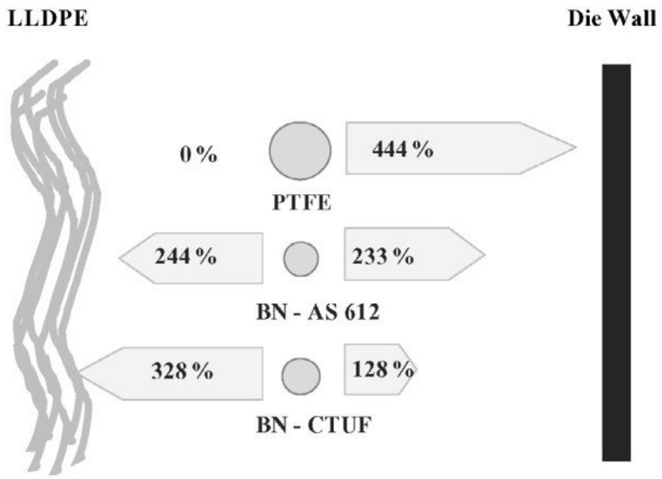


***Figure 2.11.*** *Schematic presentation showing relative affinity values of PTFE and BN particles for PE-LLD and die wall (Rathod & Hatzikiriakos 2004).*

Fluoropolymer PPAs are the most commonly used processing additives in the PE extrusion. Other processing aids include stearates, silicon-based additives, hydro-branched polymers, and supercritical fluids. Newly discovered and promising boron nitride (BN) powder along with fluoropolymer PPAs are discussed below. Understanding the working mechanism of PPA helps to comprehend the complete picture of the slippage promoting die surfaces.

### Fluoropolymers

The most common PPA for a sharkskin-prone PE-LLD is a copolymer of vinylidene fluoride ($VF_2$) and hexafluoropropylene (HFP). The $VF_2$ comonomer has a very electronegative fluoride which makes the monomer a dipole. The resulting monomer has a strong attraction with the oxides in the die steel, and thus a uniform layer of coating is gradually deposited on the steel surfaces. Flow rate, dispersion quality, particle size, and concentration affect the PPA performance. A simple coating model in presented in Fig. 2.12. It has been noticed that the PE extrudate has no trace of PPA on the surface which suggests that there is a clear interface between the coating and the polymer flow. (Stewart 1993; Kharchenko et al. 2005)

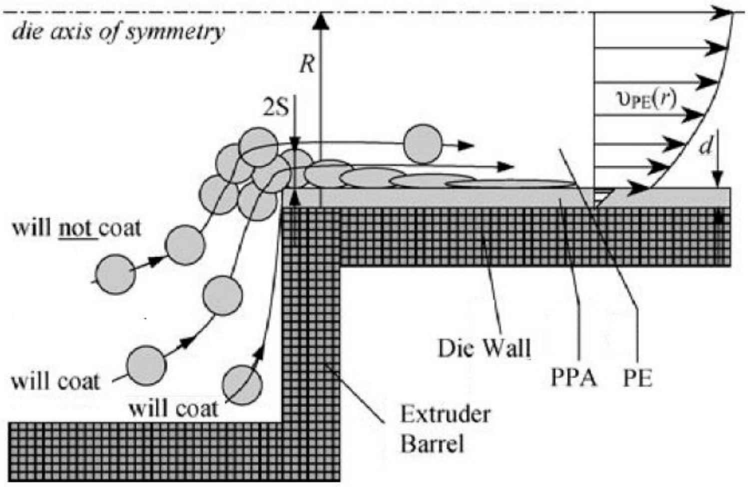


***Figure 2.12.*** *Schematic representation of the PPA coating process. It assumes that a PPA droplet (radius S) will coat the die if it is flowing down the die closer than 2S from the surface due to (modified from Kharchenko et al. 2003).*

PPAs are worthless if they do not effectively coat the die wall, so it is important to know what factors have an influence on the coating rate. One factor is higher affinity of the fluorinated PPA for an oxidated metal wall compared to the polymer melt, and thus PPAs migrate to the die wall from the polymer melt. This is the case for nonpolar hydrocarbons, such as PE, but polar polymers, like polyesters, with higher affinity to the metal wall will not be displaced from the wall, leading to PPA malfunctioning. (Kharchenko et al. 2005)

Optical microscopy has been utilized to image the coating process of the fluoropolymer PPA with transparent die walls (e.g. quartz or sapphire). A thin, lubricant layer was obtained with an addition of PPA as expected. Furthermore, a formation of downstream streaks was noticed which decreased the shear stresses even more. (Kharchenko et al. 2005) Dubrocq-Baritaud and coworkers studied the localization of slip for the fluoropolymer coated die surfaces. They concluded that the slip takes place between the PPA coating and the bulk flow as only small concentration of PPA particles was found on the extrudate surface. If the slip would happen between the metal and the PPA, the extrudate should have larger amount of PPA on the surface. However, the finding of small amount of PPA on the extrudate surface testifies that the coating wears a little over time. In the same study, a directional surface roughness perpendicular to the flow direction was found to catch and hold PPA particles better which improved the coating rate of PPA. (Dubrocq-Baritaud et al. 2011b)

### Boron Nitride

Boron nitride is a thermally stable and chemically inert solid with a structure resembling that of graphite. In addition to delaying and eliminating flow instabilities like sharkskin and stick-slip, BN has been found to substantially postpone gross melt fracture which has not been achieved with fluoropolymer PPAs. Until recently, BN has been mainly used as a foam-nucleating agent in most commercial applications for fluoropolymer foams. (Achilleos et al. 2002)

The effect of BN depends on particle type, size, and dispersion. The small crystal size (0.1 µm) worked better by delaying flow instabilities for higher shear rates compared to larger crystals (10 µm). Because the BN crystals agglomerate, the real particle size for small and large crystals were about 9 and 225 µm, respectively. However, the agglomerates were broken back into crystals and were dispersed in the twin-screw extrusion. Especially interesting for this work, also a hot-pressed BN die was used to investigate flow instabilities. The die was compacted at temperatures up to 2000 °C and pressures up to 140 bar. The BN die was found to be effective in promoting slip and suppressing extrudate distortions compared to tungsten carbide die. This was stated to be the first time a BN die was used as a processing aid utility. (Lee et al. 2003)

In conjunction with particle size and dispersion, surface energy of BN powders plays a significant role in eliminating melt fracture. A small amount of boron oxides have a detrimental effect on BN performance. The oxides increase the polar component of surface energy of polymer melt which leads to a weak affinity to the die wall. Without affinity to the wall, BN cannot form a lubricating coating. (Hatzikiriakos 2005)

### 2.4.3 Wear of Die Coating

Die coatings, especially those of fluoropolymer, wear over time in the extrusion process. Quite surprisingly, there are only a few research reports on the polymer melt induced wearing. A lot of tribological measurements of coatings have been made but the mechanism by which the wearing happens differs from one other. The fundamental difference is that the tribological measurements are done between solids whereas the wearing (in this study) should be evaluated between solid and fluid. A couple of studies are presented below to elucidate what have been published so far.

A study by Kazatchkov revealed interesting result when PP was extruded through a PTFE coated die. The shear stress was gradually reduced (to nearly half of the initial value) after each identical and subsequent runs resulting in easier processing (Fig 2.13). This indicates that the initial coating was imperfect and after an induction time of more than one hour it was smoothened out. PTFE coating is usually casted as solution from which the solvent is evaporated. It is very likely that this technique leaves micropores on the coating which might explain the behaviour encountered. However, the mechanism by which the pressure reduction is achieved remains unknown. It is conceivable that the same mechanism that smoothens the initially porous surface causes the wearing of the coating. (Kazatchkov 1994)

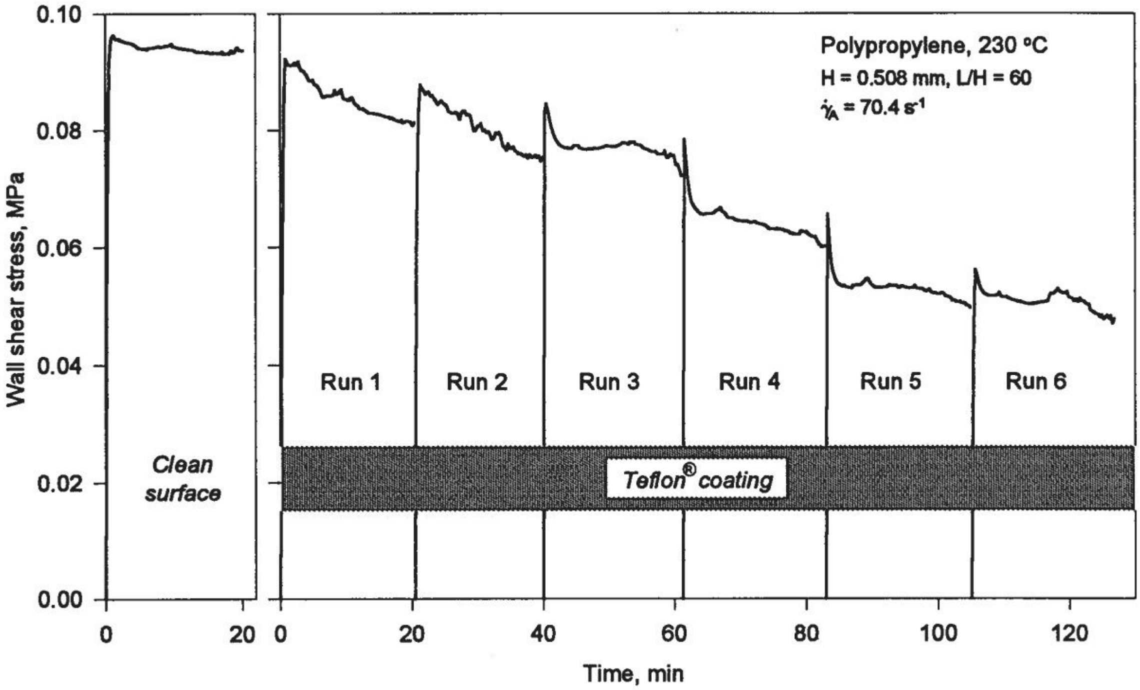


***Figure 2.13.*** *Shear stress development in the extrusion of polypropylene through a PTFE coated die. Each run represents the extrusion of a fixed amount of polypropylene (Kazatchkov 1994).*

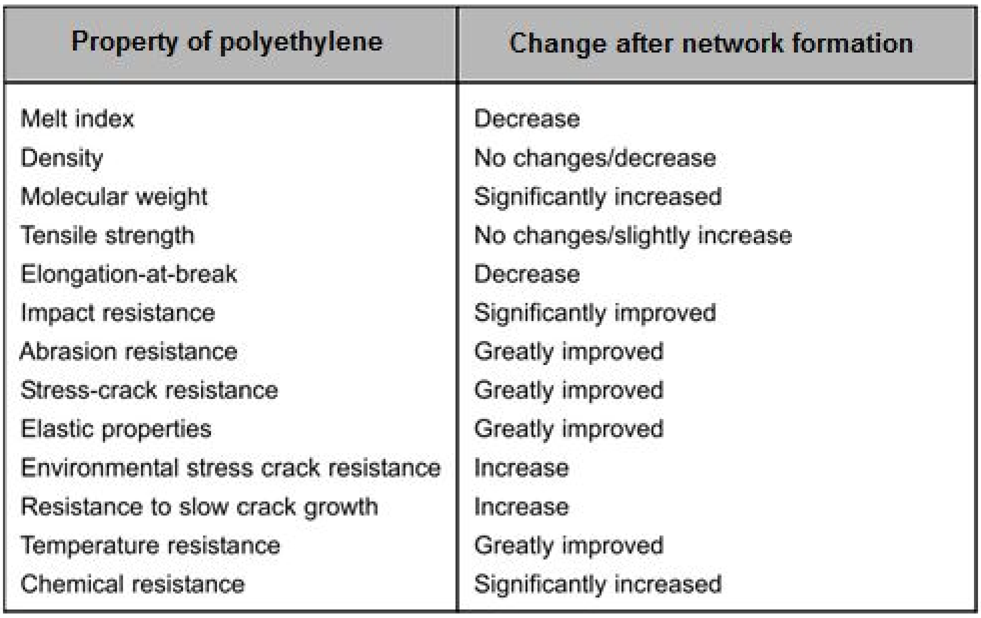
Cunha et al. studied the wear behaviour of chromium nitride based coatings with a special device attached to the injection molding machine. They used polyamide 6.6 with 35 % of glass fibre because of its highly abrasive and corrosive nature. The volume of removed coating was measured with a profilometer to describe the wearing. Physical vapour deposition of chromium nitride coating gave the best results with no detectable wearing whereas more traditionally nitrided and plated coatings showed distinctive wear. Even though a special made device was used, no plausible data or means of measuring the wear was attained. The results were left open to various interpretations and only comparative conclusions could be drawn. (Cunha et al. 2000; Cunha et al. 2002)

# 3 MATERIALS AND METHODS

## 3.1 Materials

Polyethylene (PE) is the most widely used polymer in the world. Its diverse properties and low price make it tempting choice for many purposes. However, the low upper service temperature of ordinary PE limits the usage under stresses at temperatures above 100 °C. Many properties can be improved by modifying the molecular structure of PE. The molecular structure becomes less mobile when direct links and bonds are formed between the carbon backbones of molecular chains. Cross-links occur at random intervals along the chains. Changes in properties are presented in Table 3.1. Modification of polyethylene changes its nature from thermoplastic to thermoset. (Morshedian & Hoseinpour 2009)

***Table 3.1.*** *Changes in properties when polyethylene is modified (modified from Morshedian & Hoseinpour 2009).*



| Property of polyethylene | Change after network formation |
|---|---|
| Melt index | Decrease |
| Density | No changes/decrease |
| Molecular weight | Significantly increased |
| Tensile strength | No changes/slightly increase |
| Elongation-at-break | Decrease |
| Impact resistance | Significantly improved |
| Abrasion resistance | Greatly improved |
| Stress-crack resistance | Greatly improved |
| Elastic properties | Greatly improved |
| Environmental stress crack resistance | Increase |
| Resistance to slow crack growth | Increase |
| Temperature resistance | Greatly improved |
| Chemical resistance | Significantly increased |

There are several methods to modify PE including azo, peroxide, and silane as a chemical methods and the radiation as a physical method. Peroxide modification is the most common method and was also used in this study, and it is accordingly introduced here. In this method, peroxide based chemicals are incorporated within the polyethylene compound and they initiate the formation of carbon-carbon links to create a cross-linked network. The peroxide initiator decomposes at higher temperatures and liberates a free radical that abstracts hydrogen from the polymer chain to produce a polymer free radical (Fig. 3.1). This highly reactive radical will bond with another free radical of the same or different chain. Dicumyl peroxide (DCP) is widely used cross-linking initiator. During the cross-linking reaction between DCP and PE, methane gas is released as a by-product. (Tamboli et al. 2004; Morshedian & Hoseinpour 2009)

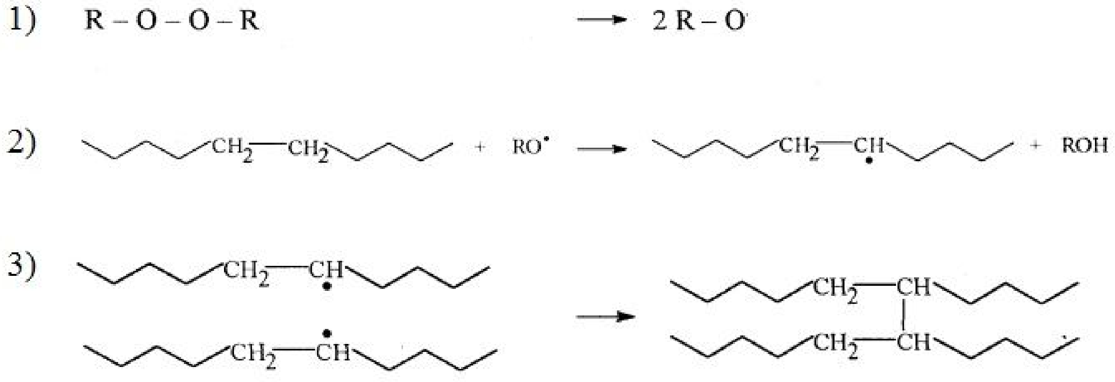


***Figure 3.1.*** *Schematic presentation of cross-linking of polyethylene in three steps (Tamboli et al. 2004).*

Cross-linking of polyethylene in the extrusion process was checked according to SFS-EN 579:1993. The standard specifies a method for the determination of the degree of cross-linking of cross-linked polyethylene pipe by solvent extraction. A modified polyethylene test piece was immersed in boiling pure xylene for 8 h using a reflux condenser (Fig. 3.2). After vacuum drying the test piece was weighted and the proportion by mass of insoluble material was calculated. The percentage of insoluble material is used to express the degree of cross-linking. The required degree of cross-linking, according to ASTM Standard F 876:1993, is 65−89 %. Solvent extraction method proved the cross-linking degree of 65 %. The test piece was collected at the highest throughput rate of 15 kg/h to guarantee that the polyethylene would cross-link on all throughput rates. (SFS-EN 579 1993)

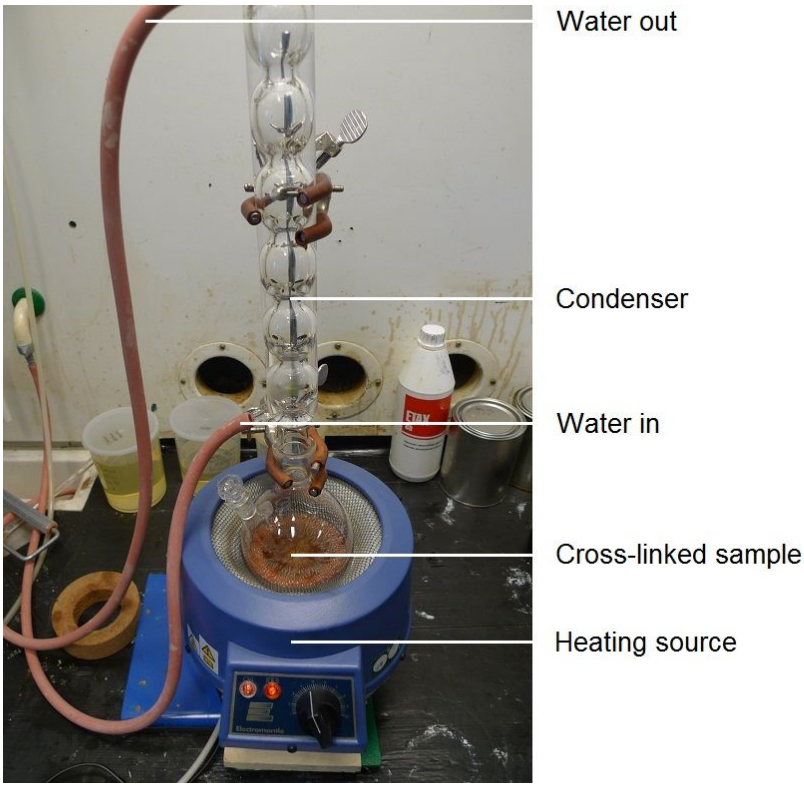


***Figure 3.2.*** *Reflux condenser apparatus for determination of cross-linking degree.*

The polyethylene grades used in this study were a high molecular mass, high density polyethylene (PE-HD) and its modified counterpart (PE-mod) especially designed for production of pipes. PE-HD grade has melt flow rate (190 °C/21.6 kg) of 10 g/10min and melting range of 100–140 °C. Cross-linking agent (i.e., peroxide) is added to the other grade which produces modified polyethylene (PE-mod). Both grades were in powder form. Before and after PE-mod extrusion, PE-HD was extruded to prevent PE-mod blocking the extruder die or the cone extruder.

## 3.2 Extrusion Apparatus

Extrusion experiments were carried out using a cone extruder (Fig. 3.3 and Fig. 3.4) equipped with a die designed to measure melt pressure and force. Cone extruder differs significantly from conventional screw extruders. The device was originally invented by Kari Kirjavainen in the late 1980's. Development project was launched together with NK Cables, Nextrom, and VTT to apply the technique in industrial scale. A few years later Conex® cone extruder was registered and commercial production started. Conex® cone extruder model 300-1 was used in this study (see Appendix 1). (Häkkinen 1999, Kirjavainen 1989)

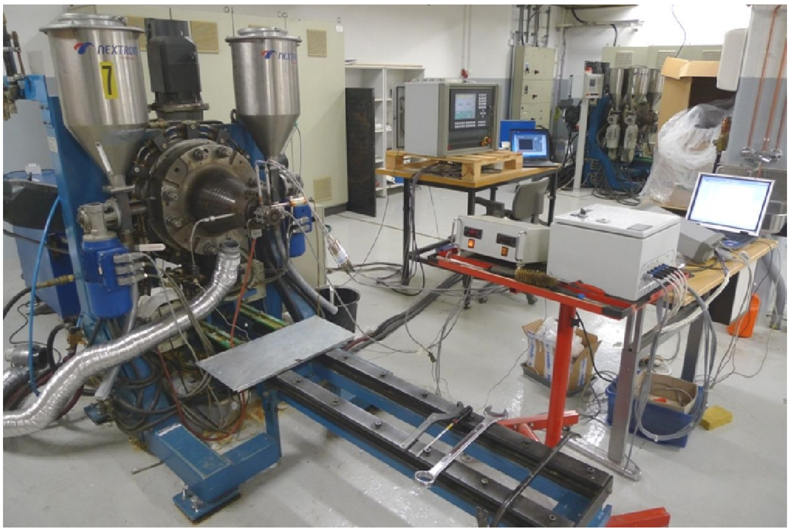


***Figure 3.3.*** *Extrusion test facilities.*

Cone extruder consists of conical screws (rotor) and stationary barrels (stator). The raw material in solid form is fed between the fixed stators and rotating rotor. The throughput rate is controlled with feeder screw speed in contrast to conventional screw extruder in which extruder screw speed determines the throughput rate. Material feeding to inner and outer sides of the rotor may be separate to create multiple layers. Temperature control in stators is managed with heating bands and rods. Machined spiral channels on the surfaces of rotor and stator help the melt flow efficiently towards the die. No complicated die structures are needed to manufacture hollow profiles or multilayer products. By increasing the number of stator-rotor-modules the material layers can be increased. One remarkable advantage of the cone extruder is that the final extrusion pressure is not created until at the end of the extruder just before the extrusion die. Other unique features are reduced residence time, effective mixing properties, and better mechanical properties of the pipe product because no weld lines are formed. (Revisio 00443d 1999, Kirjavainen 1989)

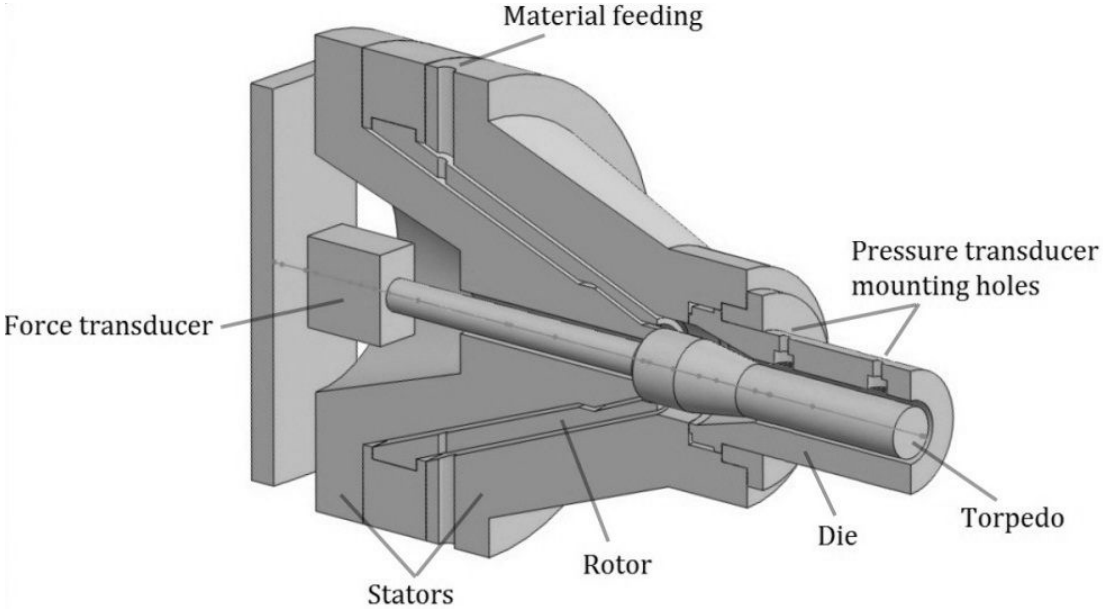


***Figure 3.4.*** *Schematic presentation of Conex 300-1 cone extruder with the measurement die (components are not in scale).*

## 3.3 Measurement Die

The measurement die (Fig 3.5) was designed in the previous study by Ville Kalapudas. The annular die was made of tool grade stainless steel and machined by Työkalu Kostamo Oy (Tampere, Finland). The measurement die was originally intended to be able to manufacture samples of PE-mod pipe as well as to measure the flow behaviour, hence, the annular design. The die has length (L), outer ($D_2$) and inner ($D_1$) diameter of 141, 32, and 26 mm, respectively (see Appendix 2 for detailed CAD drawing). Large length of the flow channel means a high pressure drop. This gives a good resolution for comparison between different coatings as long as the extruder has torque to extrude at sufficient throughput rate.

The die housing was attached onto the end of the cone extruder with a retaining plate like any other extruder die. Because of the conical structure of cone extruder no traditional mandrel structure was needed to suspend the torpedo inside the die. The die was centred in the middle with centring bolts. Design of the die enables simultaneous measurements of force and pressure. Normal force imposed to the torpedo (or mandrel) by the action of flowing polymer melt was possible to measure owing to the deviant structure of the cone extruder and annular die. The normal force was measured with a strain gauge force transducer (TB5-500kg, Lahti Precision Oy, Finland) which was mounted to the torpedo with a connecting steel bar. The force transducer signal was recorded with a sensor interface (PCD-300A, Kyowa Electronic Instruments, Tokyo, Japan) which was connected to a laptop with an analysis software (PCD-30A, Kyowa).

The die was heated to 230 °C with a 500 W mica nozzle band heater with a diameter of 62 mm and a width of 85 mm. Band heater covered the entire die surface visible after mounting it to the cone extruder. Heat loss was prevented with a glass fibre tape which was wrapped around the band heater. Cross-linking was intended to accomplish during the extrusion through the extruder die at elevated temperature. Satisfactory degree of cross-linking of polyethylene was confirmed with a method described in Chapter 3.1.

Pressure drop was measured with two Dynisco (model: MDT 462H-1/2-5C-15/46) melt pressure transducers with the output voltage of 0–10 V and pressure range of 0–500 bar. The distance of the measurement points was 60 mm (at distances 20 and 80 mm from the die exit). The pressure signals were transferred to a laptop by a signal conditioning box and an Agilent 34970A data acquisition unit. The data was gathered on the frequency of 0.5 Hz. The pressure drop is a subtraction of two simultaneous pressure measurements. No entrance pressure drop correction is needed because the pressure is measured inside the die. In fact, the pressure drop can be determined with only one pressure transducer when the exit of the die is assumed to have zero pressure (0 bar) which in this case is true.

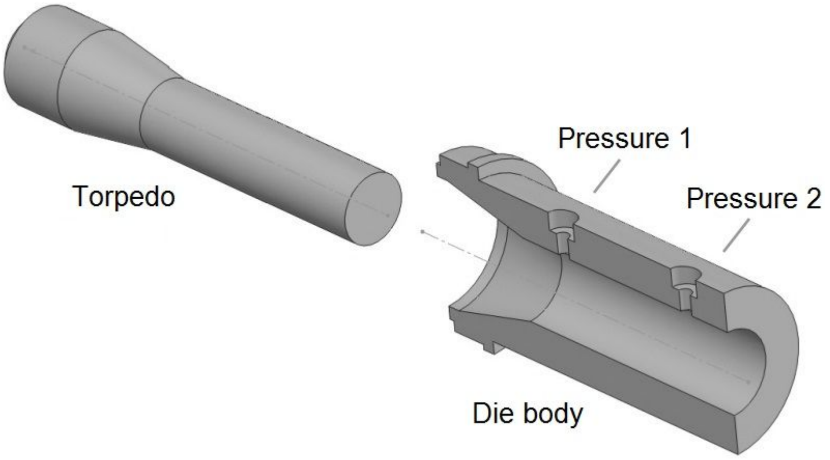


***Figure 3.5.*** *The measurement die constructions used in the pressure drop and normal force measurements. The die body is sectioned for easier observation.*

A die consisting of two halves with the same dimensions as the above-mentioned measurement die was also made to be able to apply more complicated surface treatments. The die consisting of two pieces was also machined by Työkalu Kostamo Oy. The die was constructed of two pieces so that the inside surface could be exposed, and the coating could be applied on the surface.

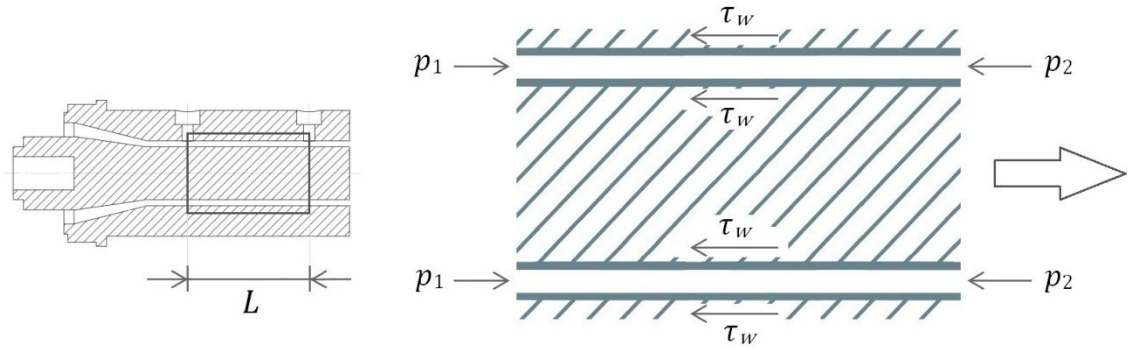


***Figure 3.6.*** *Schematic presentation of a force balance in the course of flow through an annular die.*

Results from the force and pressure measurements are in direct relationship. A force balance equation can be written from a schematic presentation in Fig. 3.6 as follows

$$p_1 \times A_p - p_2 \times A_p - \tau_w \times A = 0, \tag{1}$$

where $A_p$ is the cross-sectional surface area of the flow channel on which pressure has an effect. Wall shear stress ($\tau_w$) is exerted by the flowing polymer melt on the surrounding surfaces. In this determination, the surface area, $A$, is the combined surface area of torpedo and inner surface of the die body in the examination region. Wall shear stress can be determined from Eq. (1) after substitution of surface areas

$$\tau_w = \frac{\Delta p\ (R_0 - R_i)}{2L}, \tag{2}$$

where $R_0$ and $R_i$ are radii of the inner die body and torpedo, respectively. The pressure drop driving the flow is presented as $\Delta p$ (i.e., $p_1 - p_2$) and the distance of pressure drop measuring points is $L$. The force acting on the torpedo of length $L$ can be obtained as

$$F = \tau_w \times 2\pi R_i L, \tag{3}$$

where $F$ is the normal force applied to the torpedo which in this case was measured with the force transducer. However, the presented determination of $F$ does not take the complex geometry of the measurement die into account. Eq. (3) holds true only in the highlighted examination region seen in the Fig. 3.6.

The following assumptions have to be fulfilled to satisfy the presented determination. Relationship between $\tau_w$ and $F$ is only valid if the structure of the melt is homogenous. PE-mod is very problematic material for rheological measurements because its viscosity changes when flowing over the die surface. If yielding accurate rheological data was the primary goal, polymer with known viscosity profile should have been chosen. In the experiments, PE-mod was used whence its melt viscosity changes continuously inside the die because of gradually forming network of cross-links. For this reason it is expected that the measured and calculated values does not correlate well.

In addition, isothermal conditions are presumed in the determination. In the experiments, PE-mod is heated to desired temperature only inside the die because otherwise cross-linking would cause problems inside the extruder. Temperature inside the extruder was kept below the cross-linking temperature. Thus, another assumption of the determination is violated when temperature increases along the die length. Isothermal conditions should also apply to the wall surfaces which are in contact with PE-mod melt. Lack of a separate heating unit inside the torpedo may cause more deviation.

However, the scope of this Thesis was not to provide accurate rheological data but to study the flowing behaviour of PE-mod in extruder die. Using PE-mod as extrusion material provided invaluable data for one of the research problems: wear of the coating. This could not have been achieved with any other extrusion material. Comparative study of the coatings could be satisfyingly executed by maintaining the extrusion parameters, temperatures, and other variables constant.

## 3.4 Die Coatings

Measurements were done with six coatings: two fluoropolymers, hard chrome with fluoropolymer, boron nitride, boron nitride electroless nickel, and metal oxide. Pictures of all the die coatings is shown in Fig. 3.7. For many chosen coatings very little is known about how they would work for a certain polymer extrusion purpose. Interactions in the polymer melt−coating interface are still not well understood, as discussed earlier. Properties like non-stick, good release, high lubricity, low-friction, and good wear resistance were used to search coating options. High temperature stability was one prerequisite as extrusion temperature reaches 250 °C in industrial production. Also, especially demanding environment for extruder die posed by PE-mod melt has to be taken into account. Chemical resistance may prove crucial in long-term usage. Some of the coatings had to be chosen without previous knowledge of their function in polymer processing environment.

*Figure 3.7. Coatings on the surface of torpedo from left to right: fluoropolymer coatings 1 and 2, hard chrome plating with fluoropolymer (3), boron nitride (4), boron nitride electroless nickel (5), and metal oxide (6).*

Most of the coatings were made by industrial coating companies which do not share exact knowledge of their coatings or coating techniques because they are technical business secrets or otherwise confidential. It makes the in-depth analysis more challenging and various methods were used to study the coatings in wear tests. Comparative study between the coatings was based on pressure drop and normal force measurements only. Two coatings, namely boron nitride and boron nitride electroless nickel, were made in the premises of Department of Materials Science in Tampere University of Technology.

### 3.4.1 Fluoropolymer Coatings

The fluoropolymer coating 1 is composed of the blend of PTFE and PFA. Thickness of the coating was reported to be about 60 µm. The other fluoropolymer coating consists of only PTFE. This coating is referred to fluoropolymer coating 2.

### 3.4.2 Hard Chrome Plating with Fluoropolymer

Standard electroplating procedure was used to apply a thin layer of chromium onto a steel surface. As a consequence of the chrome plating a network of small macro-cracks are formed. The network of macro-cracks is used to interlock the fluoropolymer deposition onto the chrome plating. The fluoropolymer in question was PFA. PFA was sprayed on the hard chrome plating and then cured in an oven at 360 °C. Curing of the PFA coating improves wear resistance and adhesion to the base material. Thickness of the hard chrome plating is about 20 µm and PFA coating ranges between 20 and 30 µm. Basically, the coating is a fluoropolymer coating if the outermost layer does not wear off. The coating was chosen because of its good wear resistance and slip promoting properties.

### 3.4.3 Boron Nitride Coating

Boron nitride coating was applied as a water based paint on the die and torpedo surface. Boron nitride is recommended by the manufacturer for a use with thermoplastics and elastomers for improved die release. Boron nitride coating was kindly provided by Momentive Performance Materials Quartz GmbH (Geesthacht, Germany).

First, the die parts were thoroughly cleaned with ethanol. The die parts were heated to 80 °C to aid drying and promote adhesion. Then a thin layer of BN paint was sprayed with an air-pressurized spray gun at a distance of about 20 cm. Each layer was allowed to dry thoroughly before applying subsequent layers to prevent cracking and flaking, as suggested by the manufacturer. Multiple layers were applied. This method produced a complete covering coating with white matte look to it. The BN paint was thinned with water to 1:1 dilution for easier spraying. Mixing was done using a paint mixing paddle attached to a power drill.

### 3.4.4 Boron Nitride Electroless Nickel Coating

Nickel coating doped with boron nitride particles was applied using a glass lined plating tank with an agitation pump (Fig. 3.8). BN particles need constant agitation to keep them in suspension, hence, the use of agitation pump which circulates the suspension. Electroless plating is an autocatalytic process and no external source of electric current is needed. The electroless nickel process simply entails mixing together nickel solutions and boron nitride particles, heating them close to the boiling point, and then placing the die parts in the glass lined tank. Boron nitride particles are bonded all over the surface of the nickel providing the coating unique properties. The die parts are removed from the suspension when appropriate coating thickness is achieved. The coating has a matte satin look.

*Figure 3.8. Facilities for application of electroless nickel coating with boron nitride particles.*

Boron nitride electroless nickel kit from Caswell Inc (Lyons, USA) was used. It is an all-inclusive package for small-scale coating applications. Provided solutions and boron nitride suspension were mixed together and the parts were immersed in the suspension once the temperature of 85 °C was reached. Coating thickness of about 5 µm was achieved in 30 min.

### 3.4.5 Metal Oxide Hard Coating

Metal oxide coating was chosen due to the low coefficient of friction and excellent wear properties. Surface roughness of the coating is the lowest (0.13) of the chosen coatings. It was also the only metallic coating which would form a metal-polymer interface in the die. Being an exceptional metallic coating in dry sliding environment in respect of wear resistance and friction coefficient, it is interesting to gain knowledge of the behaviour in solid-melt interface studied in this work. Above mentioned hard chrome plating have a fluoropolymer layer on top of the metallic coating making it more of a polymer coating.

## 3.5 Experimental Procedure

The extruder die represented in Fig. 3.5 was used in the extrusion experiments. The cone extruder was heated for about 1 h before extrusion to melt all the polymer between the stators from previous extrusion experiments. First, a high density polyethylene (PE-HD) was extruded at low screw and rotor speeds to prevent overloading the cone extruder. Screw speeds were gradually increased to reach the slowest throughput rate of 5 kg/h. When extrusion process of PE-HD was stabilized at throughput rate of 5 kg/h, PE-HD was replaced by modified polyethylene grade.

Throughput rates were checked by weighing a polymer sample over a predetermined period of time at stabilized flow rate. Pressure drop and force measurement values were monitored to estimate stabilization of flow. A period of 30−60 min was extruded with constant parameters to guarantee a steady flow of the polymer. Three samples were taken to confirm the precise throughput rate. Throughput rates of 5, 10, and 15 kg/h were used corresponding to wall shear rates of 11, 22, and, 33 1/s, respectively. Maximum throughput rate was limited to 15 kg/h due to torque limitations of cone extruder because of the relatively long measurement die. Torque values of the cone extruder had to be monitored especially when throughput rate was increased because of the transient increase in mass flow rate at the time of the change. Used extrusion parameters can be found in the extrusion logbook (Appendix 3).

Extensive experiments were executed before the tests with chosen coatings begun. These experiments were a good and mandatory preparation to get used to the cone extruder operation and see how PE-mod behaves at different throughput rates. Some problems with the cone extruder and the measurement die had to be solved before the experiments. Problem with overheating on the outer stator was fixed with an external forced-air blower to improve heat transfer. Also, sufficient die temperature to initiate chemical reaction in PE-mod was discovered in these preliminary experiments.

## 3.6 Wear Characterization

The measurement die with fluoropolymer coating 1 was tested also in a separate wear test. PE-mod was extruded non-stop for 48 h at constant throughput rate of 15 kg/h. In addition to on-line pressure drop and normal force measurements, post-extrusion analyses for the coating were made using scanning electron microscopy (SEM), optical profilometer, infrared spectroscopy (IR) and differential scanning calorimetry (DSC). On-line measurements provided data throughout the test and enabled evaluation of the wearing in respect of time. Microstructure of coating and wear mechanism were investigated in post-extrusion analyses.

### 3.6.1 Pressure Drop and Normal Force Measurements

Pressure drop and normal force measurements were recorded throughout the wear test of 48 h. Pressure and force data were gathered continuously and transferred through a data acquisition system to monitor the performance of the die coating. The same test equipment was used as described in Chapter 3.3.

### 3.6.2 Scanning Electron Microscopy

Microstructure of the extrusion die coating was examined using a scanning electron microscope (SEM). Images were taken with a Philips XL 30 SEM (15 kV). A high-energy beam of electrons are accelerated and scanned through a small area of surface to generate a variety of signals. Accelerated electrons carry large amounts of kinetic energy which is dissipated into signals due to electron−sample interactions. The energy exchange between electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons, and emission of electromagnetic radiation each of which can be detected. The image is constructed from the secondary-electrons detected with a positively biased secondary-electron detector. (Reimer 1998)

SEM sample had to be taken from the die due to the relatively large size of the coated die parts. A gouge was used to cut a coating sample from the surface of the die housing. A cross-section sample was prepared by plunge-freezing the sample in liquid nitrogen and then cut into two pieces with tweezers. Samples had to be coated with a very thin layer of gold as fluoropolymers are electrically insulating materials. The specimen must be electrically conductive to prevent electrostatic charge accumulation.

### 3.6.3 Optical Profiling

Die coating was characterized by a three-dimensional optical profilometer to determine the surface roughness and topography before and after the wear test. Optical profiling is a non-contact method that utilizes white light interferometry for high resolution 3D surface measurements. The basic principle of interferometric measurement is to combine reflected light from a reference mirror and from a sample to produce interference fringes, where the contrast fringe occurs at best focus. (P/N 980-085) Close-up topographic visualization of worn surfaces enables careful study of wear patterns that helps to understand how the coating wears. Additionally, surface roughness values can be used to evaluate the correlation with pressure drop values.

A Wyko NT1100 3D optical profilometer (Veeco Instruments, Inc, Tucson, USA) was used to measure the coating with three objectives (5×, 20×, and 50×). Surface measurement was taken on top of the die body which was placed on a sample stage of optical profilometer. Image and surface roughness analyses were performed using Wyko Vision 3.44 software.

### 3.6.4 FTIR Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to study die coating from the wear test. The principle of IR spectroscopy is to recognize different molecule vibrations and rotations by beaming an infrared light through or at a sample. The radiation is absorbed by a molecule when the molecule vibrates at the same frequency as that of IR radiation. Different types of bonds and functional groups absorb IR radiation at certain wavelengths, and thus, can be identified. (Kendall 2007) For this reason, IR technique enables to qualitatively analyse the presence of various chemical bonds in the die coating. This helps to understand the changes taking place during extrusion.

IR spectra were recorded on a Bruker Tensor 27 spectrometer (Bruker Optik GmbH, Ettlingen, Germany) combined with a GladiATR accessory. It utilizes a dense monolithic diamond crystal. An evanescent wave is formed when an infrared beam is directed onto the crystal and it extends beyond the surface of the crystal into the sample in contact with it. Infrared radiation penetrates no more than 2 µm into the polymer coating.

Measurements were conducted before and after the wear experiment. A scalpel was used to cut a sample piece from the coating in order to ensure a good contact with the crystal ATR accessory and the sample. The IR spectrum before the test was obtained from a separate sample which was prepared in order to keep the coating intact. In both cases, 64 successive scans were recorded with a resolution of 4 $cm^{-1}$. The spectral data were processed using Bruker OPUS software.

### 3.6.5 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a common thermal analysis technique used in the field of polymer analysis. In a DSC scan the difference in heat flow to the sample and a reference (both on a separate heater) at the same temperature is recorded as a function of temperature. The temperature is increased at exactly the same rate. As the sample undergoes a physical transformation (e.g. melting or crystallization) increased or decreased heat will need to flow to it than the reference to maintain both at the same temperature. The resulting difference in heat is observed as a peak or curve in the DSC curve. The technique was chosen to obtain information about changes of chemical composition of the coating before and after the wear test. Noticeable changes in crystallization or melting temperatures could reveal information about the wear mechanism of the coating. (Menczel et al. 2009)

DSC was performed on a Netzsch DSC 204 F1 under nitrogen atmosphere (20 ml/min) with a heating rate of 10 °C/min from -20 to 370 °C. End temperature of the DSC scan was chosen well beyond the presumable melting point of fluoropolymer coating. Coating samples of 3–9 mg in solid form were placed and sealed in aluminium pans with a pierced lid. The DSC scan was made on a heating-cooling-reheating cycle for both coating samples to provide more complete characterization information beyond thermal history.

# 4 RESULTS AND DISCUSSION

Coatings are divided into two categories depending on how they succeeded in the extrusion of PE-mod: suitable and unsuitable coatings are discussed in the corresponding chapters. Preliminary extrusion before PE-mod was done with PE-HD as described in Chapter 3.5. Results of these preliminary extrusion trials are presented first.

Results from the two-day extrusion experiment of fluoropolymer coating 1 are discussed in Chapter 4.2. Post-extrusion analyses provide intriguing evidence on how the fluoropolymer coating loses its ability to promote wall slip during the extrusion of PE-mod.

## 4.1 Comparative Test

### 4.1.1 Preliminary Extrusion Trials with PE-HD

Fluoropolymer coatings proved to perform better in the extrusion of PE-HD than any other coating in the means of flow behaviour inside the die. Differences between the coatings are presented in Fig. 4.1 at throughput rate of 5 kg/h. The data was obtained before adding PE-mod in the extruder. Expected direct linear relationship was found between pressure drop and normal force as was discussed in Chapter 3.3. The differences between various coatings in the experiments are explained by the wall slip phenomenon. Lower the pressure drop, stronger the slip behaviour. The presence of fluoropolymers on the surface of die wall has been widely studied and it is well-known that such layers increase wall slip significantly compared to other surfaces. The result of the trials demonstrates this concept. (Ramamurthy 1986; Piau et al. 1995; Lahtinen 1997; Kulikov & Hornung 2004; Hatzikiriakos 2011).

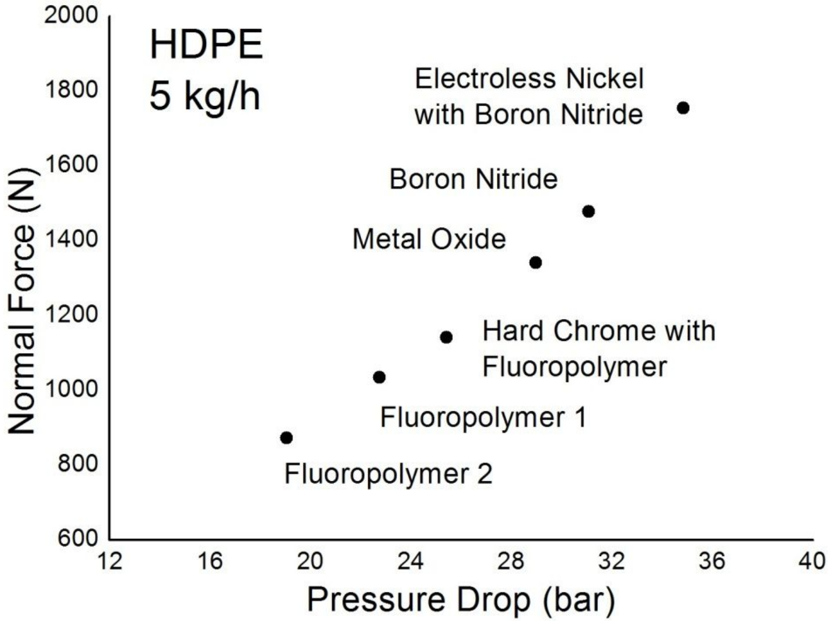


***Figure 4.1.*** *Relationship between pressure drop and normal force for all the tested coatings in the extrusion of PE-HD at throughput rate of 5 kg/h.*

Fluoropolymer coatings obtained the lowest pressure drop and normal force values. Pressure drop of the fluoropolymer coating 2 was about half of the pressure drop of the electroless nickel plating with boron nitride (EN BN): 19 and 35, respectively. Also, the difference in normal force values was the same. Similar relationship was found on the other coatings. This indicates that the distractions to the measurement procedure were successfully minimized and both the pressure drop and normal force values were reliably measured. Unquestionable differences between coatings were obtained. Small and rather ambiguous pressure drop differences in the study of wall slip have been reported in the literature. (Arda & Mackley 2005)

### 4.1.2 Suitable Coatings in PE-mod Extrusion

Extrusion trials with PE-mod could be fully conducted on three of the six coatings. Fluoropolymer based coatings were successfully tested as was planned but hard metal coatings caused problems. High melt viscosity of PE-mod built up relatively high die pressures. This would not have been a problem if shorter die was used because the pressure drop is higher the longer the die is. Now the torque limit of the cone extruder was a limitation for the trials as pressure increased as high as 250 bar for some of the coatings. However, the fluoropolymer based coatings were reliably tested and summary of the results is presented in Fig. 4.2.

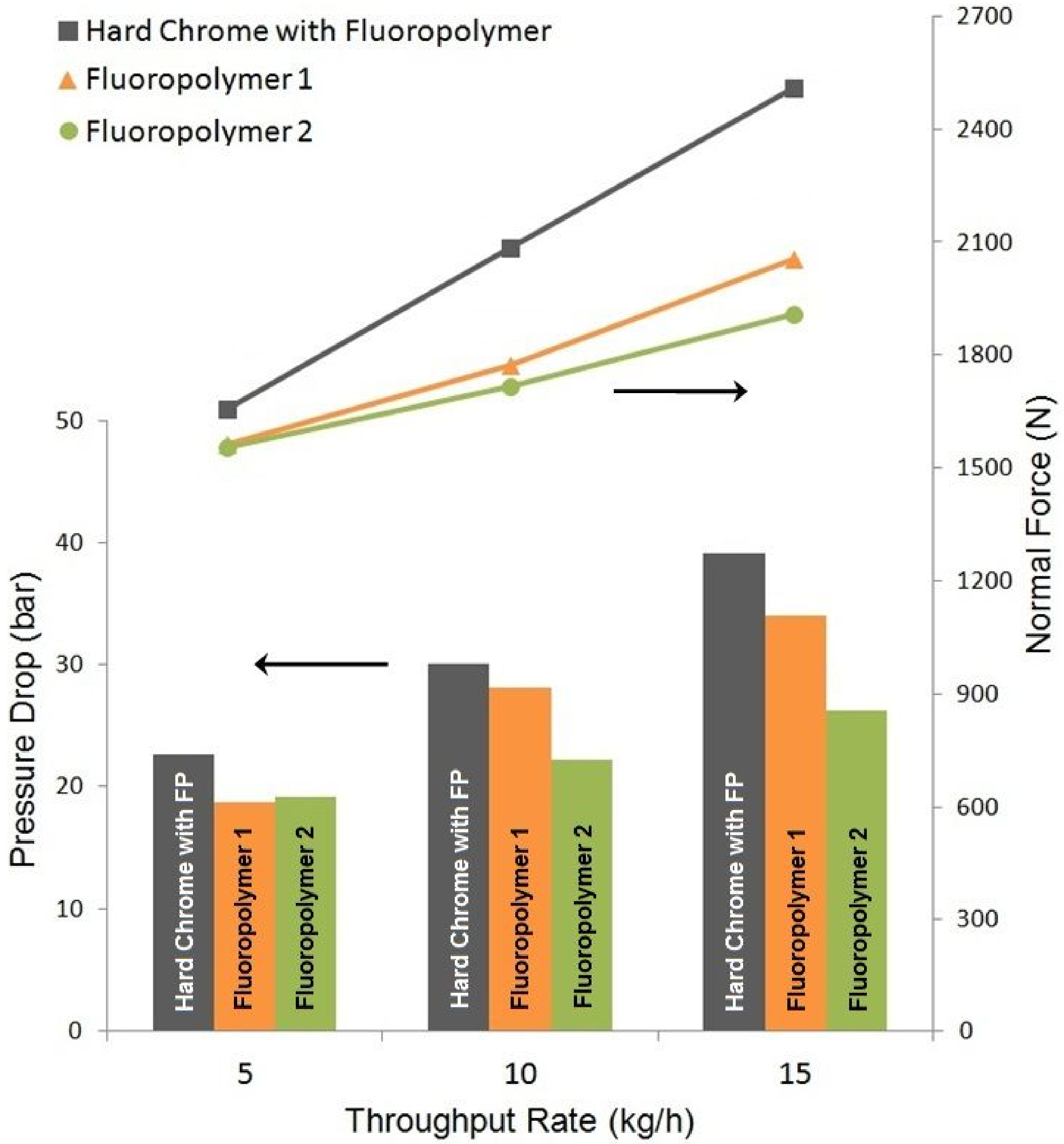


***Figure 4.2.*** *Pressure drop and normal force data of the fluoropolymer based coatings in PE-mod extrusion.*

Fluoropolymer coating 2 obtained the best results also in PE-mod extrusion trials. The lowest pressure drop and normal force indicate the strongest wall slipping behaviour. At throughput rate of 5 kg/h the fluoropolymer coating 1 had almost equal pressure drop and normal force to fluoropolymer coating 2. Difference between fluoropolymer based coatings increased with rising throughput rate and the order remained the same. At the highest throughput rate the difference between fluoropolymer coating 2 and the hard chrome plating with fluoropolymer was nearly 50 %. Corresponding difference between fluoropolymer coating 1 and 2 was about 30 %. Unfortunately, the highest throughput rate was limited to only 15 kg/h which is very small compared to industrial scale production rates. The results should be nevertheless the same with higher throughput rates because the mechanism remains the same.

The pressure drop data from PE-mod extrusion was converted to wall shear stresses by using Eq. (2) presented in Chapter 3.3. Wall shear stress data makes comparison with other published results easier as it is more widely used to describe rheological phenomena. Wall shear stress can be understood as a friction force exerted by the polymer melt on the wall. This same force was actually measured with a force transducer. Wall shear stress increases with rising flow velocity and viscosity, and decreases with larger flow channel. In this study the polymer melt−coating interface determines the wall shear stress because flow velocity, viscosity, and flow channel dimensions were kept the same in every experiment. It is good to remember that molecular characteristics (molecular weight and its distribution), processing temperature, and geometrical details have been found to affect the wall slip. (Ansari et al. 2011) Notes on these effects will be made later in this chapter.

Wall shear stress data of the PE-mod extrusion experiments is presented in Fig. 4.3. The results with PE-mod were in accordance with results from PE-HD extrusion. At all throughput rates the fluoropolymer coating 2 obtained the lowest wall shear stresses. For the extrusion of PE-mod the fluoropolymer coating 2 appears to be the best choice from the tested coatings in the light of the trials.

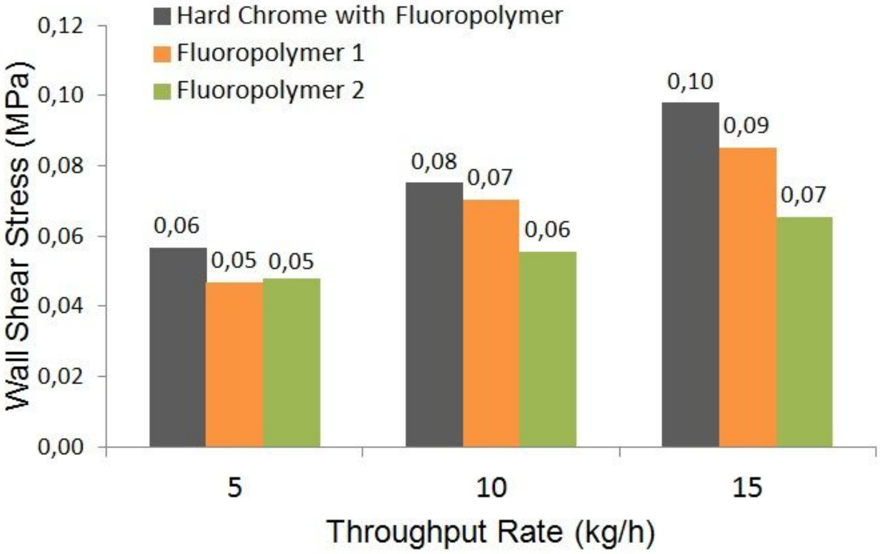


***Figure 4.3.*** *Wall shear stress data of the fluoropolymer based coatings in PE-mod extrusion.*

Wall slip phenomenon has been studied mainly in relation to flow instabilities such as sharkskin and stick-slip. Occurrence of flow instabilities limits the production rate of extrusion and therefore is of great importance in the research field. A variety of polymers and numerous construction materials of the extrusion die have been used to determine the critical shear stress value for the onset of wall slip. Onset values of 0.1–0.2 MPa are usually presented for different die materials. However, the onset of slip for fluoropolymers starts at very low shear stress. Even values below 0.03 MPa have been reported. Most of the studies have been conducted with polyethylene which is prone to flow instabilities. (Hatzikiriakos 2011)

Wall shear stresses of 0.05–0.1 were obtained for tested fluoropolymer coatings. These values are not the onset values for wall slip. These values already include the wall slipping behaviour and thus describe the magnitude of wall slipping of each coating. Kazatchkov obtained similar values of wall shear stress in the extrusion of PP with fluoropolymer coating. (Kazatchkov 1994)

PE-mod causes an additional strain on the extruder die. For this reason every test trial was started with PE-HD and changed to PE-mod when extrusion process was stabilized. Changing the extrusion material had a strong effect on the force imposed to the torpedo as shown in Fig. 4.4. PE-mod has very high melt viscosity and needs more force to be extruded compared to lower viscosity PE-HD. There was more than 50 % increase in force when the change took place. The presented data in Fig. 4.4 is taken from the extrusion trial with fluoropolymer coating 1. The pressure drop and normal force data of the complete extrusion trial can be found in Appendix 4.

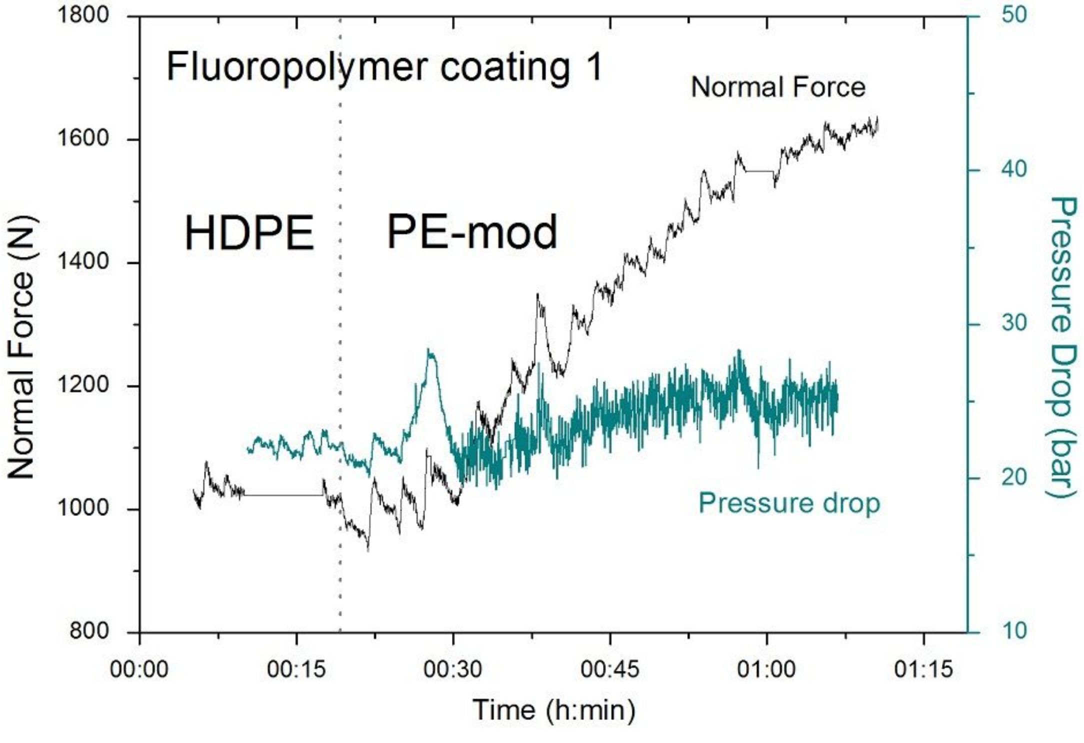


***Figure 4.4.*** *Evolution of the pressure drop and normal force in the measurement die coated with fluoropolymer 1 upon changing of the extrusion material from PE-HD to PE-mod at constant throughput rate of 5 kg/h.*

Pressure drop difference between PE-HD and PE-mod is surprisingly negligible. As the force and pressure drop are actually measuring the same behaviour they should react to changes with the same order of magnitude. Interestingly, this same trend seems to have been repeated in every separate extrusion trial (Fig. 4.1). This indicates that the wall shear stress on the surface of the torpedo is different from the wall shear stress of the die body. Fig. 4.5 presents possible flow behaviour inside the annular die which could explain the difference. As is later shown, temperature difference between the die body and torpedo may induce different wall slipping, and thus, may explain the relative difference between the force and pressure drop.

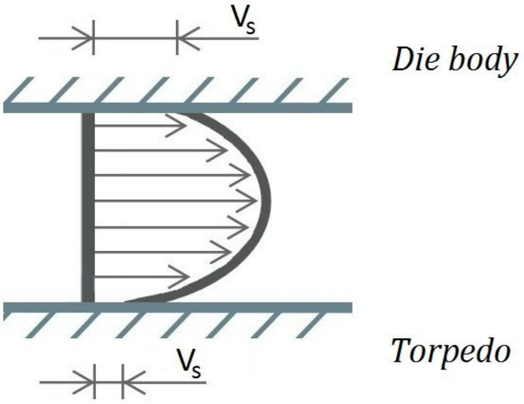


***Figure 4.5.*** *Possible velocity profile inside the annular die during comparative tests.*

It is noteworthy that as the cross-linking of PE-mod proceeds along the heated die, the flow behaviour also changes. Increasing amount of cross-links in the polymer matrix changes the polymer nature from thermoplastic to rubber-like thermoset. This change affects the wall shear stress and may be one reason why the pressure and force levels do not correlate well. At lower throughput rates PE-mod cross-links more because of the increased time under elevated temperature and vice versa.

Many difficulties with die temperature were encountered during the tests. The die was heated with a 500 W mica heater band which is powerful enough to maintain temperature in balance in the desired extrusion conditions (230 °C). However, owing to the structure of the band heater and the necessary holes for two pressure transducers, the heat did not distribute evenly in the die body (Fig. 4.6). Uneven distribution of temperature in the die body was minimized with an insulating glass fibre tape which was wrapped around the heater band.

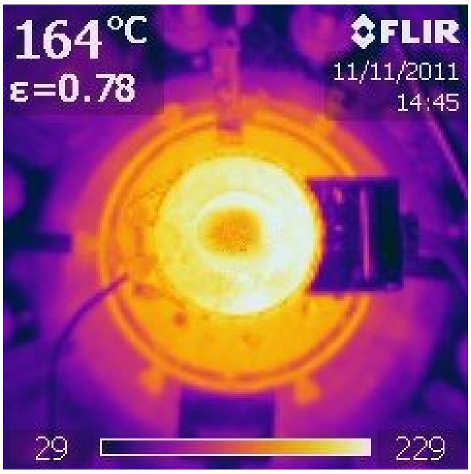


***Figure 4.6.*** *Thermographic picture of the temperature distribution in the extruder die.*

Temperature of the torpedo was much lower because it did not have a separate heating unit. Conducting heat from surrounding die and polymer melt were the only source of heat to the torpedo. In addition to thermographic photography a digital multimeter with temperature gauge was used to measure temperature from the surface of the die. Measurements on both devices confirmed that temperature difference between the die body (cylinder-shaped part of the die) and the torpedo was fluctuating around 80 °C. True temperature difference right at the interface of torpedo's surface and polymer melt is, of course, much lower because of the conducting heat from polymer melt. Multimeter measurement gauge could be positioned only in the middle of the torpedo whence the large temperature difference. Temperature difference of 20−30 °C was evaluated from the thermographic photographs. This difference is enough to affect the wall shear stress because of the changed shear viscosity of the melt. Higher temperature cross-links the PE-mod even more. In the light of this interpretation the difference in magnitude of the pressure drop and normal force curves can be understood. It is possible that the different wall shear stress induced different wall slip behaviour on the interfaces of torpedo−PE-mod and PE-mod−die body. Whether the wall slipping is stronger for PE-mod structure with more cross-links or less cross-links remains unknown.

The effect of surface roughness on wall slip phenomenon has been widely studied as was discussed in Chapter 2.2.1. A mechanical stylus device Mitutoyo SJ-201P (Mizonokuchi, Japan) was used to measure surface roughness of all the tested coatings before experiments. Optical profilometer imaging could not be used on all the coatings because of its time-consuming usage. The mechanical stylus tester is a user-friendly instrument to quickly determine an average surface roughness, $R_a$, and therefore adequate for this purpose. Results from the measurements are presented in Table 4.2. Resolution of the device is stated 0.01 µm.

***Table 4.2.*** *Average surface roughness of all the tested coatings measured using a mechanical stylus device.*

| Surface Roughness, Ra [µm] | |
|---|---|
| Metal Oxide | 0,13 |
| Steel | 0,23 |
| Fluoropolymer 1 | 0,73 |
| Fluoropolymer 2 | 0,76 |
| Electroless Nickel with BN | 1,16 |
| Hard Chrome with Fluoropolymer | 1,25 |
| Boron Nitride (BN) | 2,50 |

When comparing the surface roughness values with pressure and force data from the extrusion experiments, there seems little correlation between the two. This is partly out of line with current understanding of wall slip phenomenon. The published results are often speculative and in some cases contradictory. Surface roughness affects the wall slip but the surface nature of the coating has stronger impact on the slip behaviour. (Chen et al. 1993; Larrazabal et al. 2006a; Allal & Vergnes 2011) For example, the electroless nickel plating with boron nitride had surface roughness about 2 times smaller than better performing boron nitride coating. The same coatings with different surface roughnesses would have been tested if the effect of surface roughness was the primary research problem.

Note that there is a little difference between the surface roughness values of fluoropolymer coating 1 from optical profilometer (discussed in Chapter 4.2.2) and mechanical stylus tester. Optical profilometer and portable tester provide $R_a$ values of 0.88 and 0.73, respectively. The most probable reason for the difference is that the non-contact method of optical profilometer provides more reliable information because it does not damage the coating while measuring. The mechanical stylus can damage the coating and provide a lower surface roughness values. This is the case especially for softer coatings. For harder coatings the difference between the two methods should be smaller.

### 4.1.3 Unsuitable Coatings in PE-mod Extrusion

Full extrusion test plan was not possible to execute with metal oxide, boron nitride, and boron nitride electroless nickel coating because PE-mod adhered on the die wall. This unexpected setback left test data incomplete. However, the qualitative result was a sufficient result in itself and further examination was not needed in the scope of the Thesis. Nonetheless, an introduction on the possible reasons behind these outcomes is presented in the following chapters.

The metal oxide coating could not be fully tested because PE-mod instantly adhered on the die wall and finally blocked the entire die. The extrusion experiment was started with PE-HD in the same way as other tests. Normal force of the metal oxide coating for PE-HD was about 20 % higher than for the hard chrome plating with fluoropolymer. Higher normal force on PE-HD predicted that metal oxide coating could not perform very well on PE-mod either. Also the surface of the extrudate had badly defected appearance as shown in Fig. 4.7.

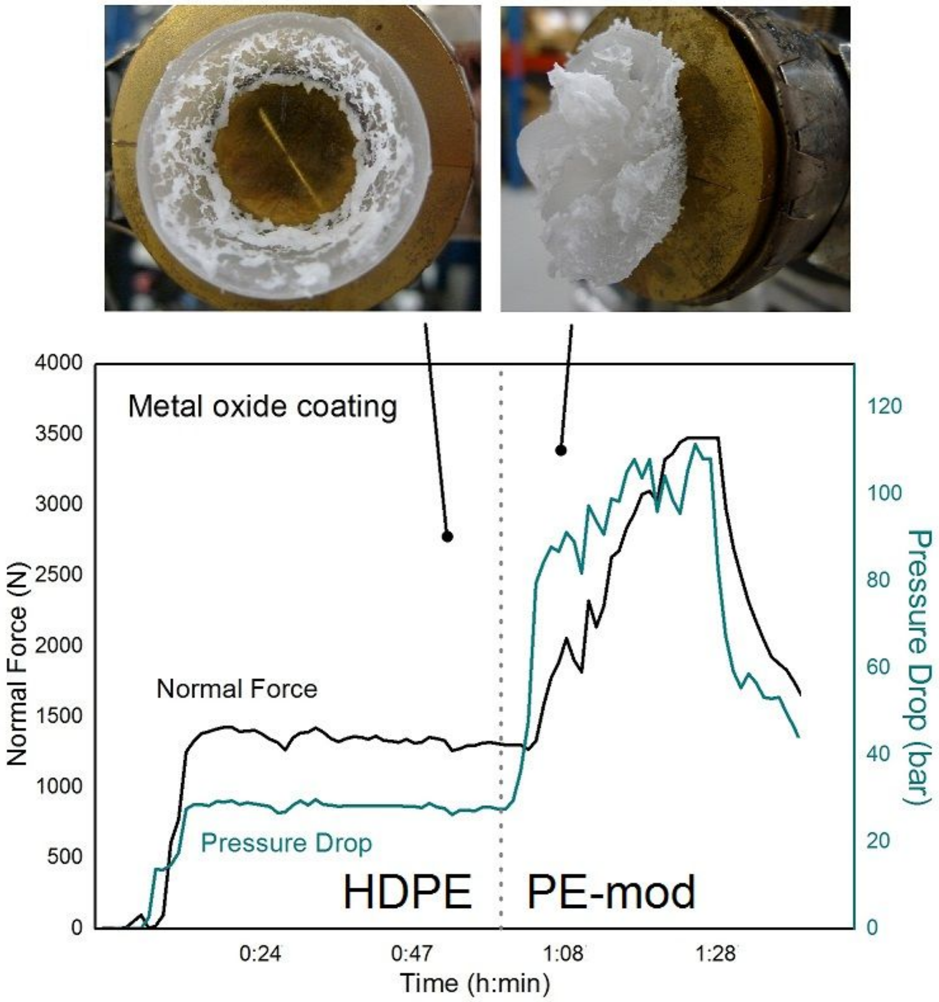


***Figure 4.7.*** *Evolution of pressure drop and normal force with the metal oxide coating at throughput rate of 5 kg/h following a complete blockade of the die. Left picture shows how PE-mod adheres on the die wall and on the right picture the complete blockade of the die.*

Once PE-mod was added to the extrusion, the force and pressure drop values shoot up. Adsorption of the extrudate got worse and as the residence time inside the die slowly increased, the cross-linking accelerated. Increasingly cross-linked PE-mod gradually blocked the flow channel of the die when the melt viscosity became too high. Stabilized throughput rate of 5 kg/h with PE-mod could not be reached at all with the metal oxide coating. Consequently, the data for the comparative study was not gathered for the metal oxide coating. In the end, the extruder die had to be removed and the cone extruder opened for cleaning. Optical profilometer images were taken from the torpedo in order to assess reasons for the poor performance (Fig 4.8).

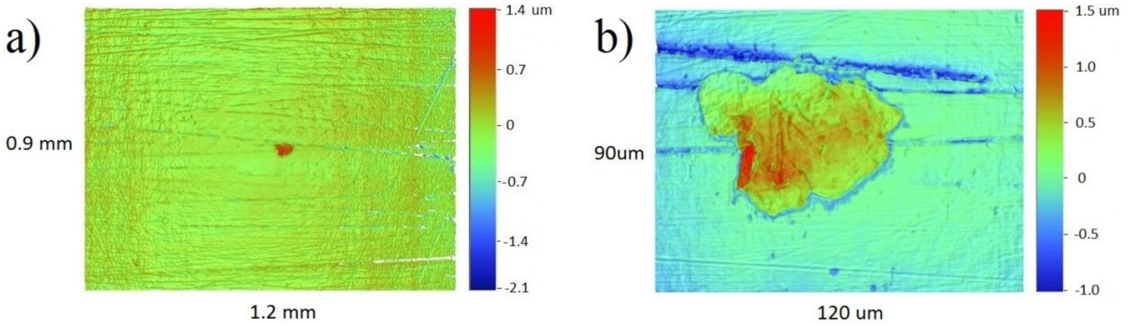


***Figure 4.8.*** *Optical profilometer images of metal oxide coating after the unsuccessful experiment. Magnifications of 20× (a) and 50× (b).*

Tiny scratches perpendicular to the polymer flow were found on the surface of the torpedo. Surface preparation or application technique of metal oxide coating are the most likely reasons for the perpendicular scratches. Small pieces of PE-mod were also found on the surface and it seems that PE-mod has adhered on the scratches. With available characterization methods the reasons for strong adhesion between metal oxide coating and polymer melt were difficult to specify. Surface energy calculations might elucidate the behaviour. These calculations have been utilized in the research of polymer processing additives' adsorption on the die wall. Contact angle values were defined between two materials from measured surface energy values. This contact angle determination proved to be useful in predicting interaction between two materials. (Rathod & Hatzikiriakos 2004)

Similar result was obtained with boron nitride (BN) coating and electroless nickel coating with boron nitride particles. PE-HD was successfully extruded at throughput rate of 5 kg/h but PE-mod adhered in the die wall and extrusion trial had to be stopped. Pressure drop and force values rose so quickly that there was no question continuing the test. Especially surprising outcome was achieved with highly promising boron nitride coating. Boron nitride powder has been widely studied and used as polymer processing additive (PPA) in the extrusion of polyolefins in the last decade. (Rosenbaum et al. 2000; Achilleos et al. 2002)

Rosenbaum et al. hypothesized that the true wall slip does not explain the enhanced processability of polyolefins when BN is added as PPA contrary to fluoropolymer based PPAs. Wall slip is usually accompanied by a significant shift towards lower shear stresses but with BN this is not the case. It was argued that BN has ability to create apparent slip in the layer adjacent to the wall due to the generation of variable viscosity zones. As BN has a high adsorption capacity for PE it is possible that BN perform well as PPA but not as die wall material. (Rosenbaum et al. 2000; Muliawan & Hatzikiriakos 2004)

Interesting studies were conducted by Lee et al. and Kulikov & Hornung who used a BN die in the extrusion of PE-LLD. The BN die improved the processability by remarkably decreasing wall shear stresses. Also, the surface defects were postponed to higher shear rates. Best results were obtained with both the BN die and incorporation of BN as PPA. Kulikov & Hornung argued that the BN die provides the highest defect-free rate of extrusion among steel, Teflon, and brass dies. Researches by Lee et al. and Kulikov & Hornung are unique because no other experimental study have been published to the author’s knowledge in which solid boron nitride die wall has been used in polyolefin extrusion. (Lee et al. 2003; Kulikov & Hornung 2004)

The chemical nature of the BN coating used in this Thesis is very similar to the BN die used by Lee and Kulikov & Horning and that’s why the outcome was surprising. Again, it is possible that the determination of surface energies might throw light on the understanding of this outcome. Here we return to the PPA study by Rathod and Hatzikiriakos (2004) in which they defined relative affinity values between two materials (Fig. 2.11). Fluoropolymer particle has strong affinity to steel die wall but very low affinity to extrusion material whereas BN particle has similar affinity for the both. In this Thesis the determining affinity would be only between extrusion material and particle (i.e., coating) because the particle material is bound to the die wall prior to extrusion in the coating process. In the light of this interpretation the outcome is understandable.

## 4.2 Wear Characterization

Two-day extrusion trial with fluoropolymer coating 1 revealed many interesting details about wear of the coating during the extrusion of PE-mod. The test trial was executed with a fluoropolymer coating because of its fast and unknown wear mechanism. The extrusion had to be stopped in the last few hours of the trial because the coating had worn unusable (Fig. 4.9).

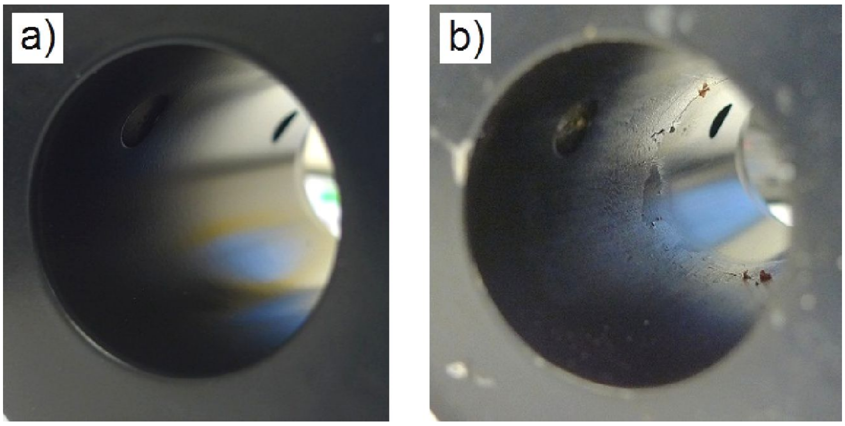


***Figure 4.9.*** *Fluoropolymer coating 1 before (a) and after (b) the extrusion experiment.*

On-line measurements were gathered with force and pressure transducers in the same manner as in the comparative tests. Pressure drop and normal force data is presented in the next chapter. Post-extrusion analyses provided insight in the wear mechanism. Post-extrusion characterization is presented in the chapters following pressure drop and force data.

### 4.2.1 Pressure Drop and Force Data

Pressure drop and normal force data is presented in Fig 4.10. Wearing of the coating is easily seen in the increasing pressure drop value. During the first 12 h the fluoropolymer coating 1 retained its properties because the pressure drop did not increase. In effect, the properties of the coating enhanced because a small decrease in the pressure drop is noticeable. Similar observation was made by Kazatchkov who noticed decrease in wall shear stress of a PTFE coating after subsequent extrusion runs with PP resulting in easier processing. The reason behind this behaviour was deduced that the coating smoothened over time. Kazatchkov's extrusion experiment lasted about 2 h. (Kazatchkov 1994) In the extrusion experiment of this Thesis there is a progressive increase in pressure drop after 12 h which indicates wearing of the coating.

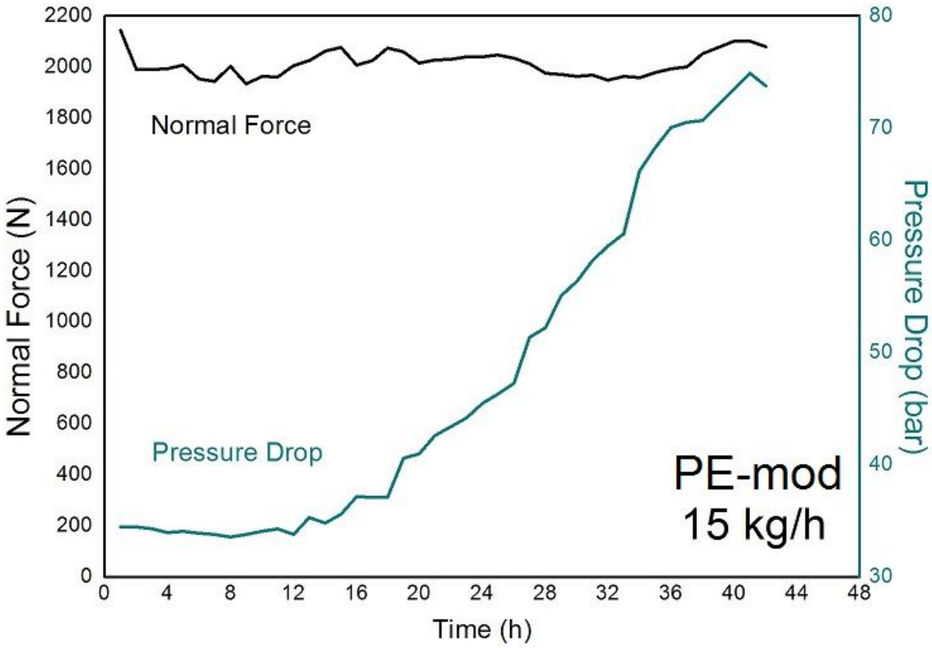


***Figure 4.10.*** *Evolution of pressure drop and normal force in two-day extrusion of PE-mod.*

It is good to remember that pressure drop data represents an average wall slip of both the torpedo and die body whereas normal force data describes the wall slip on the torpedo only. Normal force values didn't follow the values of pressure drop as was expected. Normal force remained more or less the same throughout the two-day extrusion. In the beginning the level of force was reasonable considering the pressure drop value. There are two conceivable explanations for the steady values of normal force:

One possible explanation involves the temperature difference (discussed in Chapter 4.1.2) between the torpedo and the die body. Temperature on the die body was much higher than on the torpedo and this could induce different wall slip mechanism. It seems probable that the surface of the torpedo maintained its slipping properties better than the surface of the die body. In this case, the presented flow behaviour in Fig. 4.5 would be opposite. Confirmation for this conjecture was given when the surfaces were compared before and after the extrusion by means of ocular inspection. Surface of the torpedo remained similar contrary to the die body which had very different look before and after the extrusion experiment (Fig. 4.9).

Second explanation concludes that the torpedo was stuck in the cone extruder and didn't measure the relevant force. However, this explanation does not convince because the initial force appeared correct in relation to pressure drop. Also, after the initial drop in force during the first hour there is a small noticeable increase in force during the entire two-day experiment which can be interpreted as wear.

In the literature the effect of temperature on wall slip has been found to be polymer dependent and usually relatively minimal. Hatzikiriakos and Dealy presented that the slip velocity increased with temperature for PE-HD. However, the effect was small and decreased with increasing shear stress. (Hatzikiriakos & Dealy 1992) Similar observations have been made by several authors (Wang & Drda 1997; Wu et al. 2004; Larrazabal et al. 2006a). The case with PE-mod and fluoropolymer coating 1 shown in Fig. 4.9 seems different from the investigated cases in the literature and thus they are not comparable. It looks like PE-mod have adhered only on the surface of the die body because of the elevated temperature and not on the surface of torpedo. Therefore, the normal force values have not responded which is seen as a muted response in normal force but amplified response in pressure drop.

### 4.2.2 Optical Profiling

3D optical profilometer images are presented in Fig. 4.11 at 20× magnification. The intact microstructure of fluoropolymer coating is clearly visible from the Fig. 4.11a. As a consequence of the coating technique the surface consisting of hills and valleys is formed when the particles are melted on top of each others. Particle sizes vary between 20–150 µm but most particles are approximately 100 µm. It is noteworthy that the sample before the wear test shows already some wear marks indicating a sensitive nature of the coating to mechanical wear.

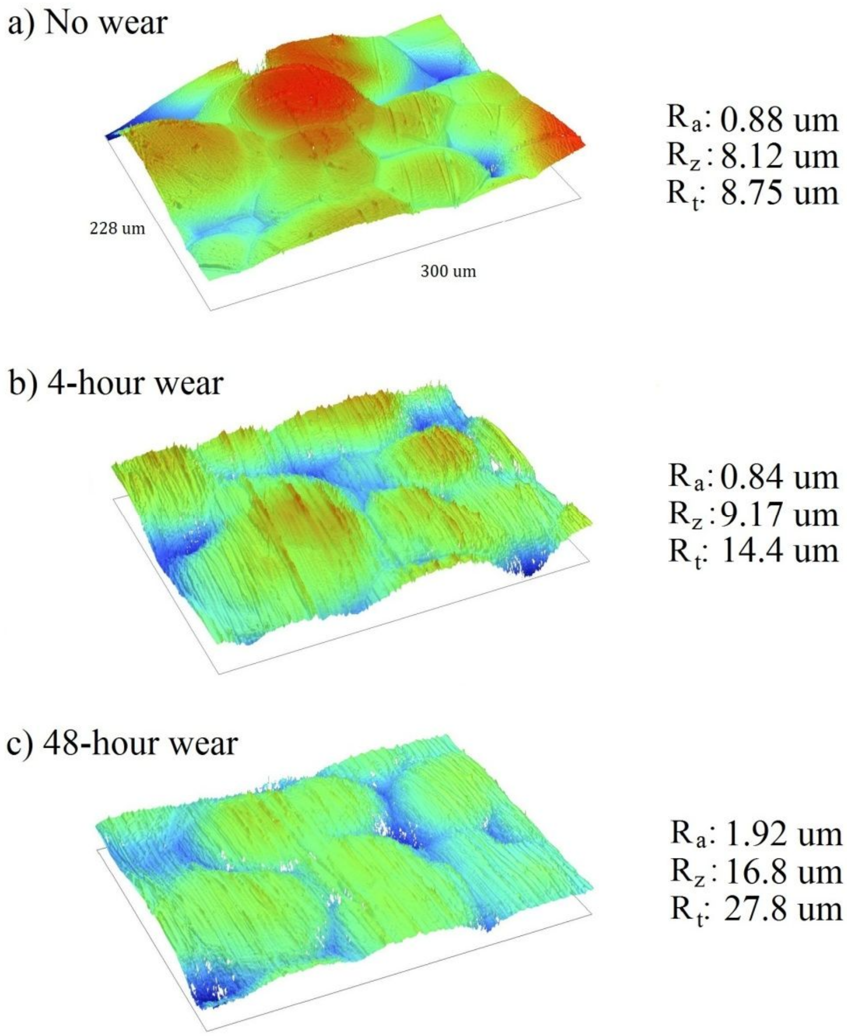


***Figure 4.11.*** *Evolution of surface roughness during extrusion of PE-mod with fluoropolymer coating 1.*

The sample after 4-hour wear is presented in Fig. 4.11b. Clearly visible wear marks have appeared in the direction of polymer flow. The hills of the coating seem to have flattened. A single wear mark resembles the outcome of a conventional pin-on-disc wear test under dry sliding conditions.

After the two-day extrusion run the sample (Fig. 4.11c) has further worn but not to an extent which could have been expected after the 4-hour wear test. The wear marks and hillocky structure is still clearly visible. It looks like the coating wears quickly in the beginning but the wear rate decreases as the extrusion continues. From the optical profilometer images it is clear that the coating loses its ability to work properly some other way than by wearing off the surface. Due to the relatively weak magnification ability of the optical profilometer imaging a further study of the wear marks with scanning electron microscopy is justified.

More importantly, the optical profilometer provides well-defined surface roughness values of $R_a$, $R_z$, and $R_t$ referring to average surface roughness, ten-point mean surface roughness, and maximum roughness height, respectively. The surface roughness values presented in Fig. 4.11 have been calculated by using the arithmetic mean average of at least three optical profilometer measurement (228 um × 300 um). Closer look at the surface roughness values reveal something the images could not. In fact, the surface roughness increases during the extrusion of PE-mod. Either the coating wears off very unevenly producing deep wear marks making it rougher or something adheres on top of the coating making it rougher.

### 4.2.3 Scanning Electron Microscopy

The die surface was analyzed by scanning electron microscopy after the two-day extrusion experiment. Because of the large size of die parts the coating had to be removed from the die surface to enable microscopy. Altogether three samples were prepared. Two samples were removed from the virgin and worn coatings and the third sample was prepared from the worn coating for cross-section microscopy. Pictures from the virgin and worn coatings are presented in Fig. 4.12.

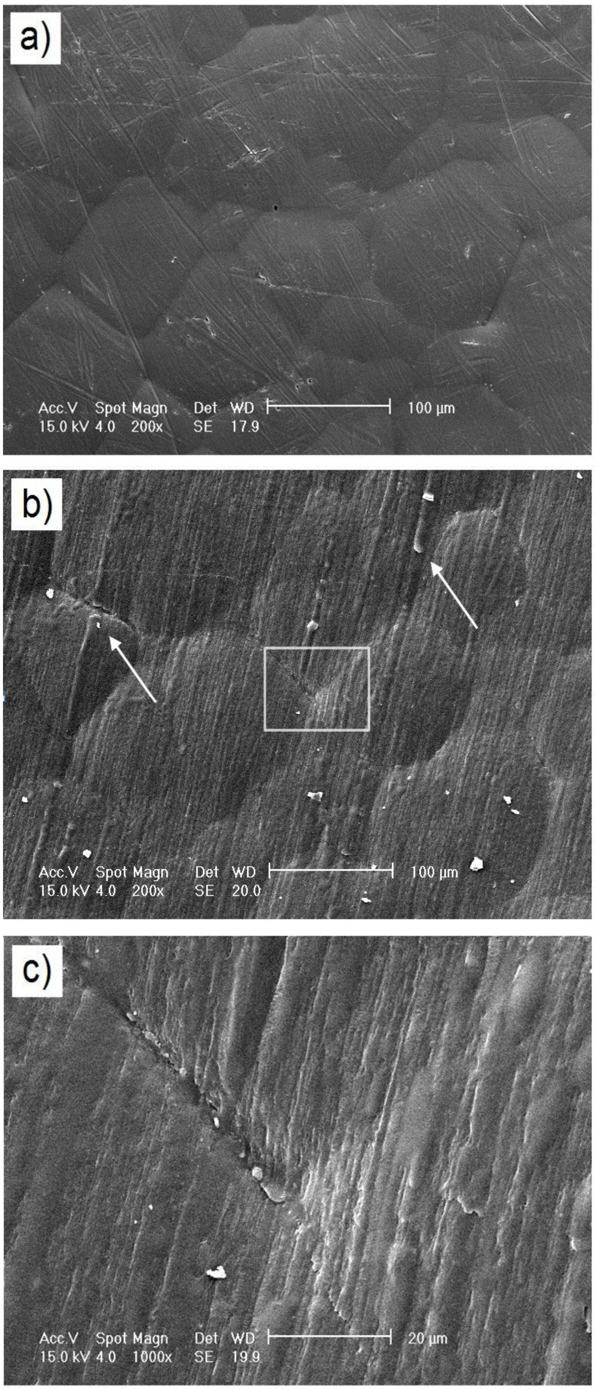


***Figure 4.12.*** *SEM images of virgin (a) and worn (b,c) coating.*

From Fig. 4.12 it looks like the coating has not eroded but some foreign matter have adhered on the surface instead. Arrows are pointing to the accumulated material. The extrusion material was the same during the entire experiment so the foreign material must be PE-mod or some components of it. The flow direction is clearly visible in the worn sample as was the case with optical profilometer images (Fig. 4.11).

The sample for cross-section imaging was prepared by freezing it in liquid nitrogen and then bent into two pieces to reveal the cross profile. The sample curled up by the time of the microscopy and no cross-sectional image was possible to take. However, the images taken from the cross-sectional sample reveal interesting details as shown in Fig. 4.13.

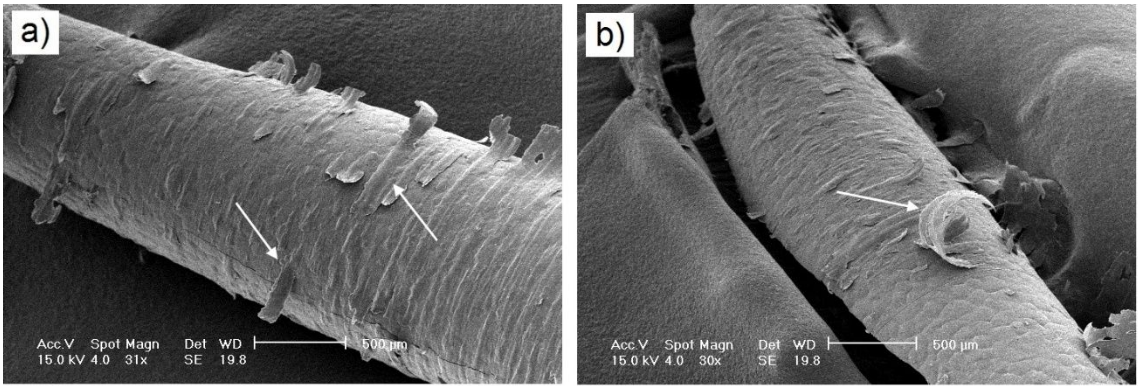


***Figure 4.13.*** *Samples of curled-up fluoropolymer coating 1.*

The structure of the fluoropolymer coating is clearly visible also in the SEM pictures. It looks like that there is another layer of matter in some parts of the coating (arrows are pointing at some of these). It is likely that the plunge-freezing of the sample in liquid nitrogen separated the other layer accumulated during the two-day extrusion experiment.

By examining the most recognized wall slip mechanism (discussed in Chapter 2.2) the accumulation of accumulated matter can be understood. Cohesive failure holds that slip results from disentanglement of chains in the bulk from chains adsorbed at the wall. The flowing polymer bulk slips over an adsorbed brush. The long adsorbed molecules are attached to the wall in many points forming loops and tails. Generally, every absorbed chain has two mobile tethered chains and motion restricting loops in the between. In the presence of flow the chain loops will eventually be squeezed against the wall by the flowing bulk and do not interact with the bulk as much as tethered chains. The tendency of chain adsorption increases with the surface energy of the wall. (Denn 2001; Tchesnokov 2005)

This explanation seems more plausible than the other slip mechanism. Adhesive failure slip mechanism holds that the polymer chains must detach from the die wall to induce slip. The elevated temperature of the die body from which the SEM samples were taken may have enhanced the adsorption of polymer chains and thus the accumulation of the extrusion material. Now the interesting question is: what is the chemical structure of these flakes? The flakes were too small to be removed with tweezers so the IR spectroscopy was done on the entire sample to determine the chemical structure of the accumulated matter.

### 4.2.4 IR Spectroscopy

IR spectra were taken from the virgin and worn coatings. IR spectra are presented in Fig. 4.14. Pronounced differences in the IR spectrum between the virgin and worn coating appear in the regions of 1300–1700 cm$^{-1}$ and just below 3000 cm$^{-1}$.

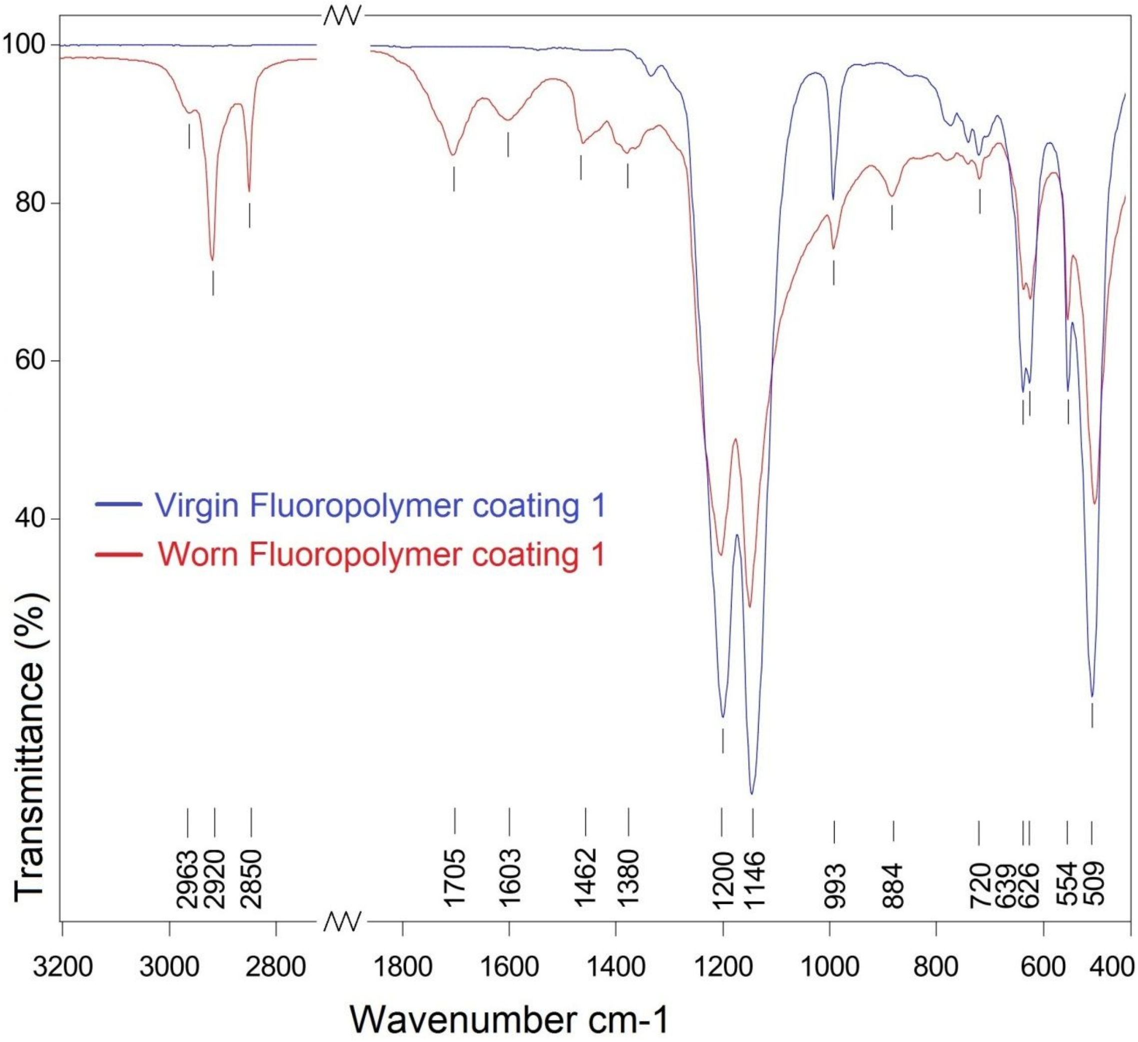


***Figure 4.14.*** *IR scan of the virgin and worn fluoropolymer coating 1.*

IR absorption bands at 2850, 2870, 2920, and 2960 cm$^{-1}$ are related to C-H bond stretching. Peaks at 2850 and 2920 cm$^{-1}$ are considerably stronger than the peak at 2963 cm$^{-1}$. This means that the sample contains many $CH_2$ groups but only few $CH_3$ groups. Confirmation for this conclusion can be made if a weak band is found at about 720 cm$^{-1}$ which comes from the rocking vibrations of $CH_2$ group. In addition, medium IR absorption bands are found around 1350–1470 cm$^{-1}$ which are bending vibrations of $CH_2$ and $CH_3$ groups. It is worth noting that the virgin fluoropolymer coating has very little or not at all hydrogen because no bands appear in the region of 2800–3100 cm$^{-1}$. (Yong-Cheng 2011)

Another difference in IR absorption bands can be found at wavelengths of 1603 and 1705 cm$^{-1}$. The difference can be explained by the oxidation of the accumulated polyethylene layer on top of the fluoropolymer coating. Oxidation is usually easy to detect because of the strong absorption by the carbonyl group around 1670–1820 cm$^{-1}$. In the presence of oxygen, polyethylene oxidizes, degrades, and cross-links. The oxygen essential for oxidation probably ends up in the extruder and extruder die with and inside the polyethylene powder. Therefore, the use of nitrogen purge blanket on the hopper may not have effect. Only antioxidants terminate the reactions. Elevated temperature and pressure are known to increase the oxidation process. (Rabek 1975; Warnar 2002) This may explain why the torpedo has not degraded as much as the die body which had higher temperature because of the poor temperature control of the die.

Presence of fluoropolymer is obvious when the peaks with highest intensity are interpreted. The peaks of the $CF_2$ symmetric stretching are much lower in frequency than $CH_2$ stretches because fluorine atoms are more massive. These peaks should appear at 1200 and 1146 $cm^{-1}$. Weaker peaks around 715–774 $cm^{-1}$ are related to $CF_2$ scissoring. CF stretching and bending bands are shown in the area of 630–640 $cm^{-1}$.These peaks are assigned to belong to the groups located in the crystallized zones of fluoropolymer. $CF_2$ twisting and bending appears at 509 and 554 $cm^{-1}$, correspondingly. (Mihály et al. 2006)

IR scan was also taken from the other side of worn coating which was attached to the steel die wall (Appendix 5). IR absorption bands in the region of 2800–3100 $cm^{-1}$ were not visible. This can be interpreted that the accumulated material only adsorbed on the surface of the coating and did not penetrate into the entire matrix of the coating.

### 4.2.5 Differential Scanning Calorimetry

Both virgin and worn coatings display similar curves with an endothermic melting peak of about 300 °C as shown in Fig. 4.15. The worn coating had melting peak 3 °C lower than the virgin coating. However, the two-day extrusion experiment did not lead to any significant change in chemical structure of the coating.

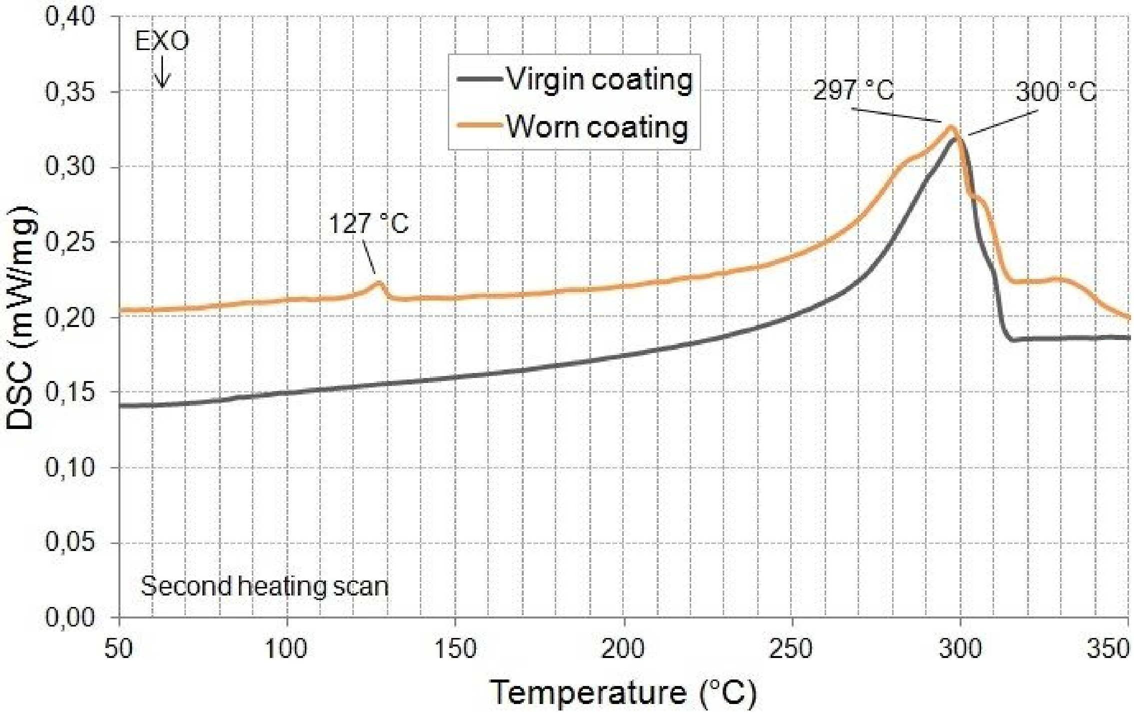


***Figure 4.15.*** *DSC curves of the virgin and worn fluoropolymer coating 1.*

Interestingly, there is a small endothermic peak at 127 °C in the DSC curve of worn coating. Corresponding exothermic peak of crystallization at 110 °C is also found in the cooling curve (Appendix 6). No such peaks are observable in the virgin coating. Small peak at 127 °C could be interpreted as a melting peak of PE-mod especially after considering the result from IR spectroscopy. Because of the weak magnitude of the endothermic peak and relatively small size of the sample (3.2 mg) further investigation is needed.

# 5 CONCLUDING REMARKS

The effects of various extruder die coatings were investigated in the extrusion of modified polyethylene (PE-mod). Based on the presented results, the following conclusions can be drawn:

1) The fluoropolymer-based extruder die coatings have been shown to perform the most desired behaviour in the comparative extrusion trials with PE-mod. Fluorinated surfaces, namely fluoropolymer coating 1 and 2, obtained the lowest pressure drop and drag force indicating the strongest wall slipping along the extruder die surface. Tendency of fluoropolymer coating 2 to sustain the wall slipping properties at increasing throughput rates was proved the most competitive.

2) Coatings consisting of boron nitride, electroless nickel with boron nitride particles, and metal oxide were found to be unsuitable for the extrusion of PE-mod. These coatings exhibited forcible sticking on the die surface which made extrusion impossible. However, strong sticking behaviour could be utilized in other applications where adhesion between solid surface and polymer melt is needed.

3) The cone extruder, which was used in the experiments, has a structure which enables measuring of the pressure drop and drag force exerted by flowing polymer melt onto the torpedo with a custom fabricated annular extruder die. The results demonstrate that the used measurement facilities are appropriate for testing different die coatings in the demanding case of PE-mod extrusion. This novel method provided the drag force and pressure drop data which to the author's knowledge have not been published before. However, by implementing several improvements suggested in the following section, yet better results could be obtained.

4) The wear mechanism of fluoropolymer coating 1 was elucidated by analysing the coating after the two-day continuous extrusion experiment. A thin layer of polyethylene was found sticking on the surface of the fluoropolymer coating 1 which had a detrimental effect on the wall slipping behaviour. It is believed that the cohesive wall slip mechanism leaves fractions of molecule chains of polyethylene anchored on the surface where they increasingly accumulate by thermo-oxidative degradation. Operating life of the fluoropolymer coating 1 could be significantly increased by reducing temperature of the die.

# 6 SUGGESTIONS FOR FURTHER RESEARCH

Extruder die used in the experiments provided simultaneous measurements of force and pressure drop. In fact, both the pressure drop and normal force describe the same phenomenon: wall slipping. This makes the measurements more reliable yet unnecessary. The pressure drop measurement is more reliable than the force measurement because it is simpler and can be executed with various structures of die. If another measurement die is constructed, it should be based on the pressure drop measurements only. Conventional type of screw extruders could be used if the measurement die would measure only pressure drop. Therefore the die could be used more widely compared to the cone extruder which is rarely used in polymer processing industry.

The use of cone extruder limited the throughput rate to relatively small rate of 15 kg/h. Only momentarily the throughput rate was increased to about 20 kg/h with PE-mod. Torque limit of the cone extruder was exceeded with greater throughput rates because of the long length of extruder die. Pressure drop increases with longer length of the die and the effect is even more pronounced with high-viscosity PE-mod. If larger throughput rates are required a measurement die with shorter length is advisable.

Temperature control of the measurement die needs to be fixed if similar measurements are planned in the future. Now the temperature of torpedo was markedly lower which had a profound effect on the wear mechanisms between torpedo and die body. Easy way to overcome this problem is to mount a heating rod with a temperature gauge inside the torpedo. In addition, temperature difference in the die body must be fixed. A heating band with better design covering the entire outer surface of the die body is needed. 500 W mica heater band used in this Thesis was powerful enough but the design was inadequate. Used glass fibre tape insulation provided temporary solution for the problem.

The annular shape of die enabled drag force measurement but made coating sample preparation more difficult. Measurement die was too large for microscopy and therefore the coating had to be removed from the die wall. This procedure could not be done without damaging the sample. If only pressure drop would be measured, another die shape could be used. For example, a slit die used in the study by Hatzikiriakos and Dealy was constructed from two pieces so that the interior surfaces could be exposed. Similar idea could be used in the scale of extruder die. Pressure transducers could be attached to the even side of the die. Also, one pressure transducer would be enough because the pressure drop can be determined between the transducer and the end of the die (where p=0) as discussed in Chapter 3.3. Multiple pressure transducers along the die length could be mounted if the effect of cross-linking degree on wall slipping needs to be characterized. (Hatzikiriakos & Dealy 1993)

The experimental study revolving around wall slip phenomenon has been conducted mainly with capillary and slit rheometers. Wall shear stress values for different coatings could be ideally determined with capillary rheometers without conducting large scale extrusion experiments with extruders. The use of PE-mod may cause problems as the cross-linking should take place exactly the same way inside the die in every experiment. The advantage of using rheometers is that they would provide reliable shear rate (i.e., throughput rate) control and more efficient way of performing measurements.

The study of coatings to induce wall slip is very difficult because one cannot resolve what is happening at molecular distances from the die surface, and thus, no mechanistic conclusions are possible. With no comprehensive understanding of the wall slip mechanism, it is difficult to rationally design new coating materials. (Migler et al. 2001) Interesting new materials not tested in this Thesis although presented in Chapter 2.4.1 include silicone rubbers, PEEK, and PEEK with BN particles. Quite surprisingly, only lately elastomers and rubbers have been introduced as a die coating option in polymer extrusion by Kulikov and Hornung. Modern synthetic elastomers like fluorinated hydrocarbon elastomers, perfluorinated elastomers, silicone elastomers, and fluorosilicone elastomers could provide positive results owing to their excellent heat stability and chemical resistance in addition to wall slip promoting properties. (Kulikov & Hornung 2004) Structured surfaces are yet to be experimented in the extrusion of polymers and may provide a new perspective on the adhesion control.

Wear characterization methods should be increased to include X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR), and equipment for determining contact angles of surfaces. XPS enables characterization of a surface layer only several nanometers thick. Chemical structure of the accumulated polyethylene could be indentified more precisely. Quantitative information about atomic composition and chemistry of the coating could be obtained. In addition, chemical and molecular characterization can be conducted using NMR. Process of choosing promising coatings for future experimentation should utilize the contact angle measurements in order to gain better understanding of interactions taking place in the solid-melt interface. This method has been successfully used in coating analyses in the literature. (Stewart 1993; Anastasiadis & Hatzikiriakos 1998; Larrazabal et al. 2006b)

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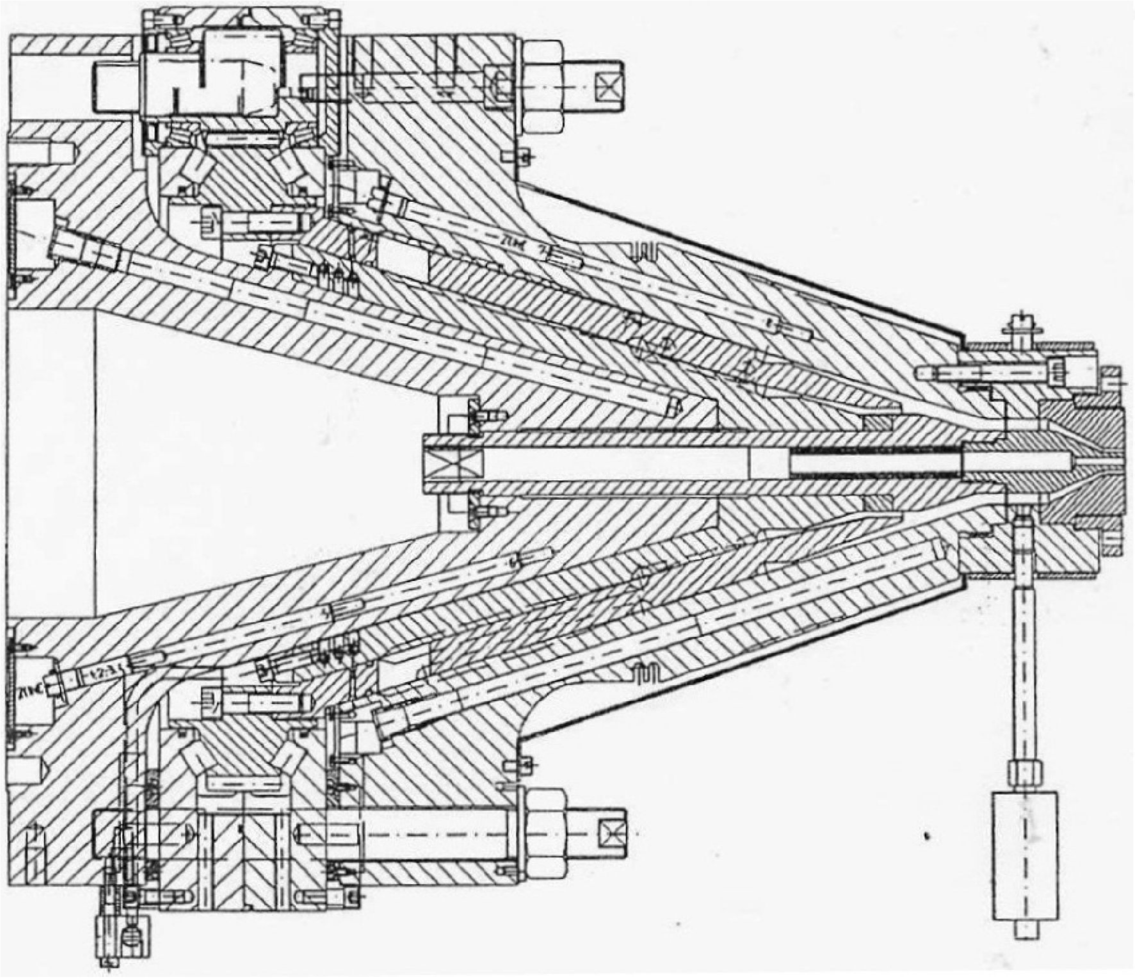
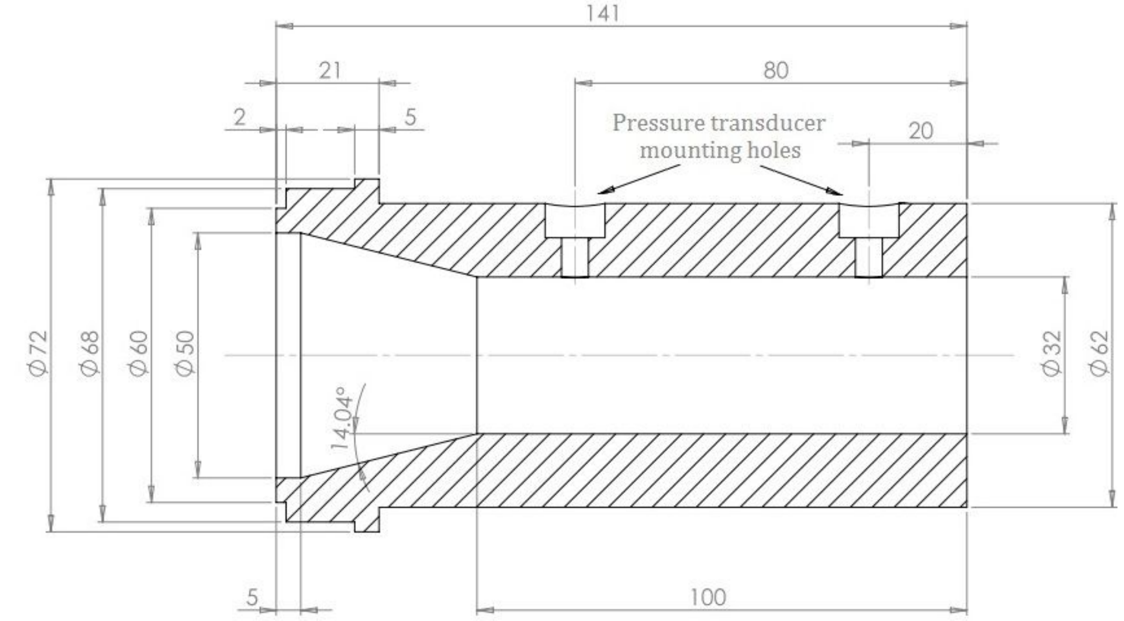
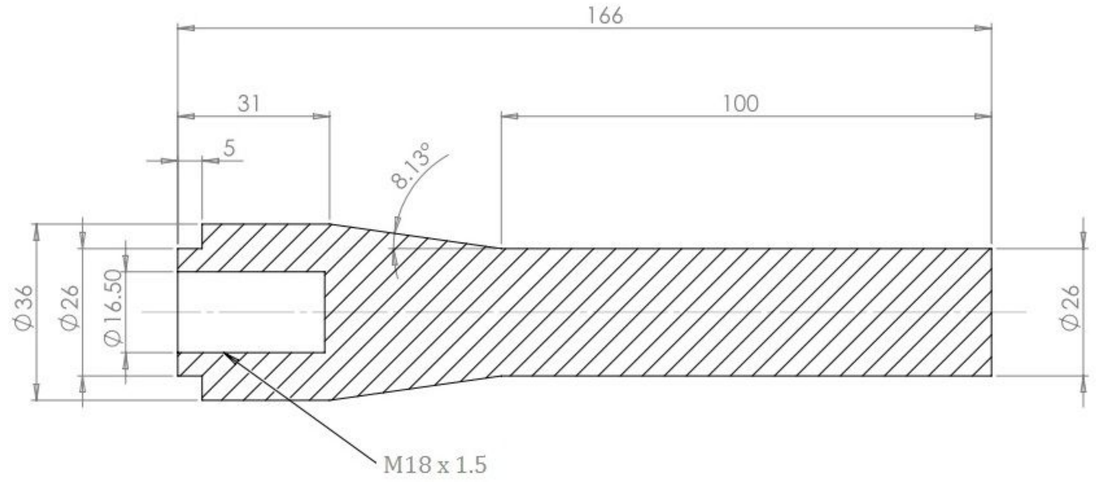
# APPENDICES

# APPENDIX 1: CONEX 300-1 EXTRUDER

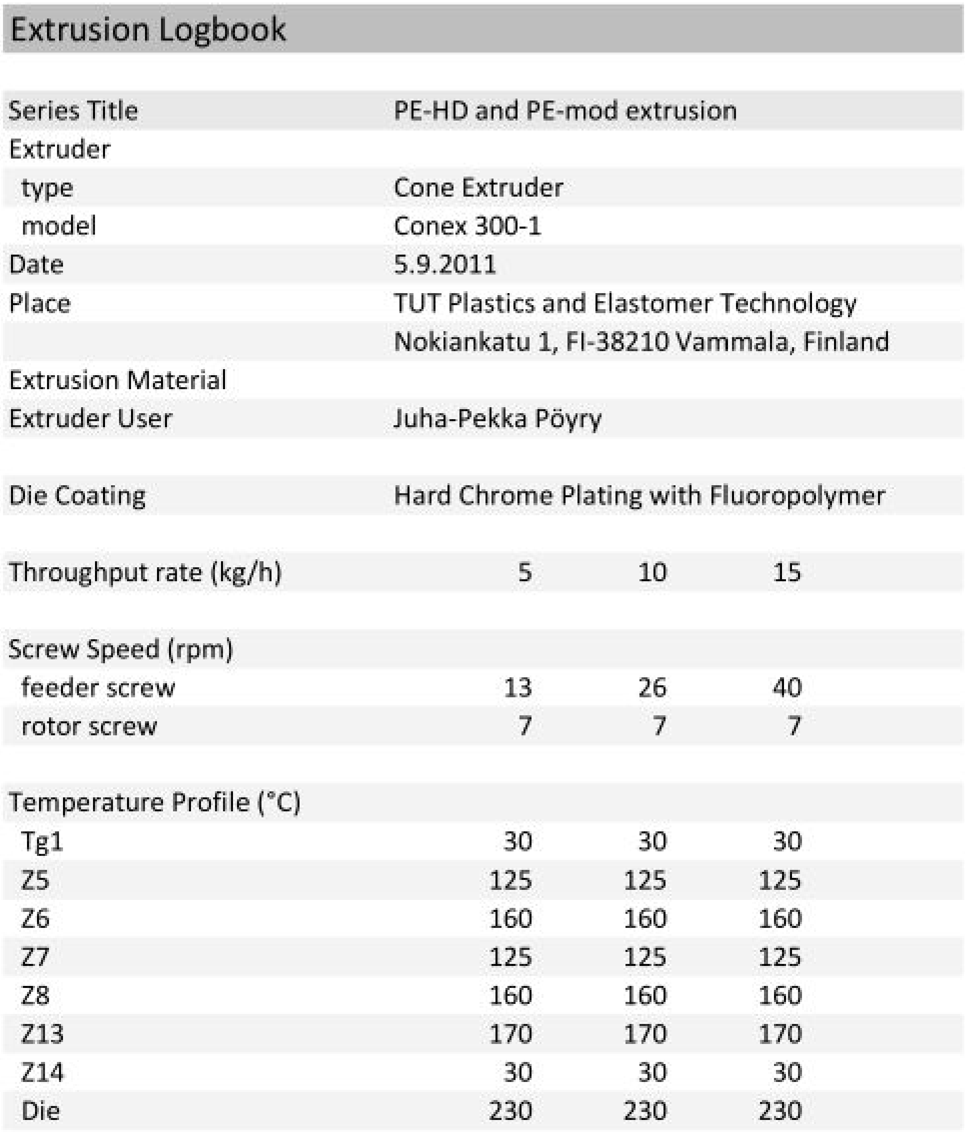


# APPENDIX 2: MEASUREMENT DIE





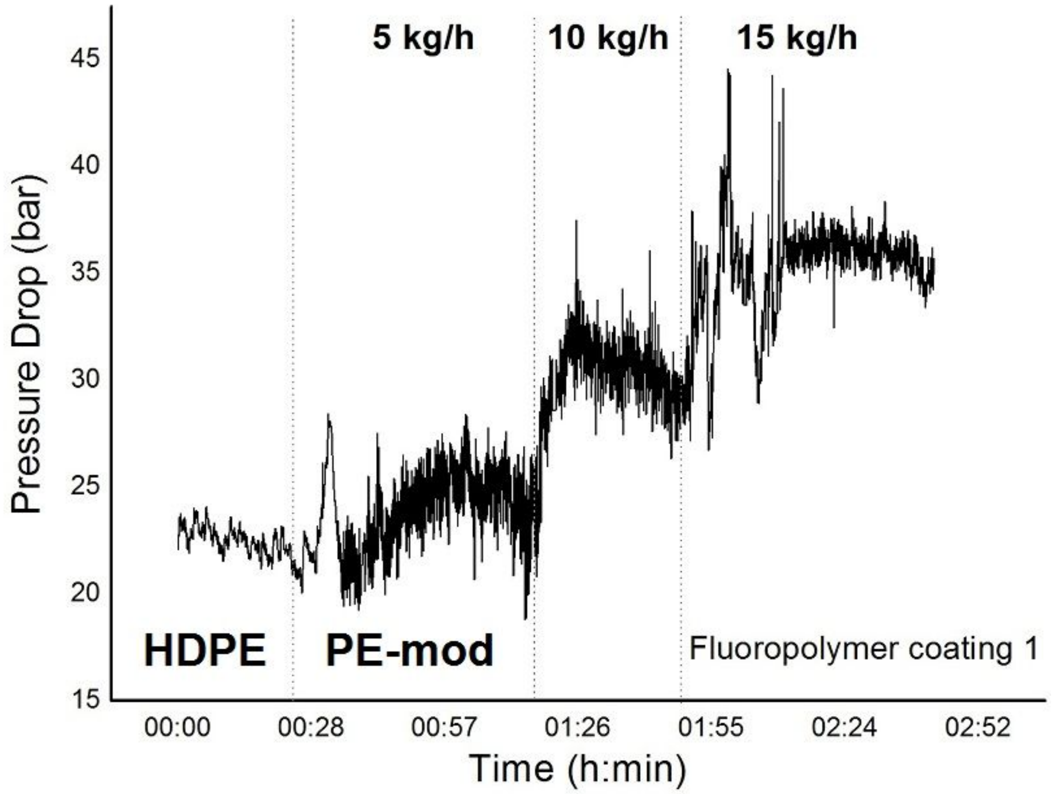
# APPENDIX 3: EXAMPLE OF EXTRUSION LOGBOOK

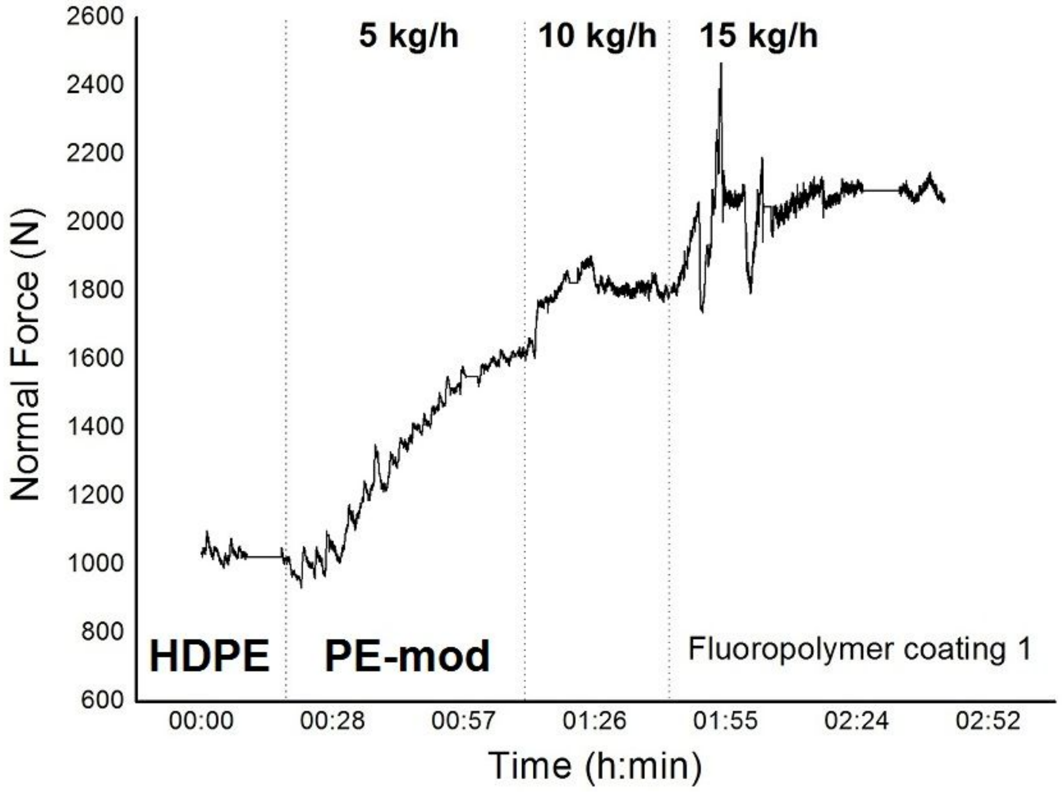


Extrusion Logbook

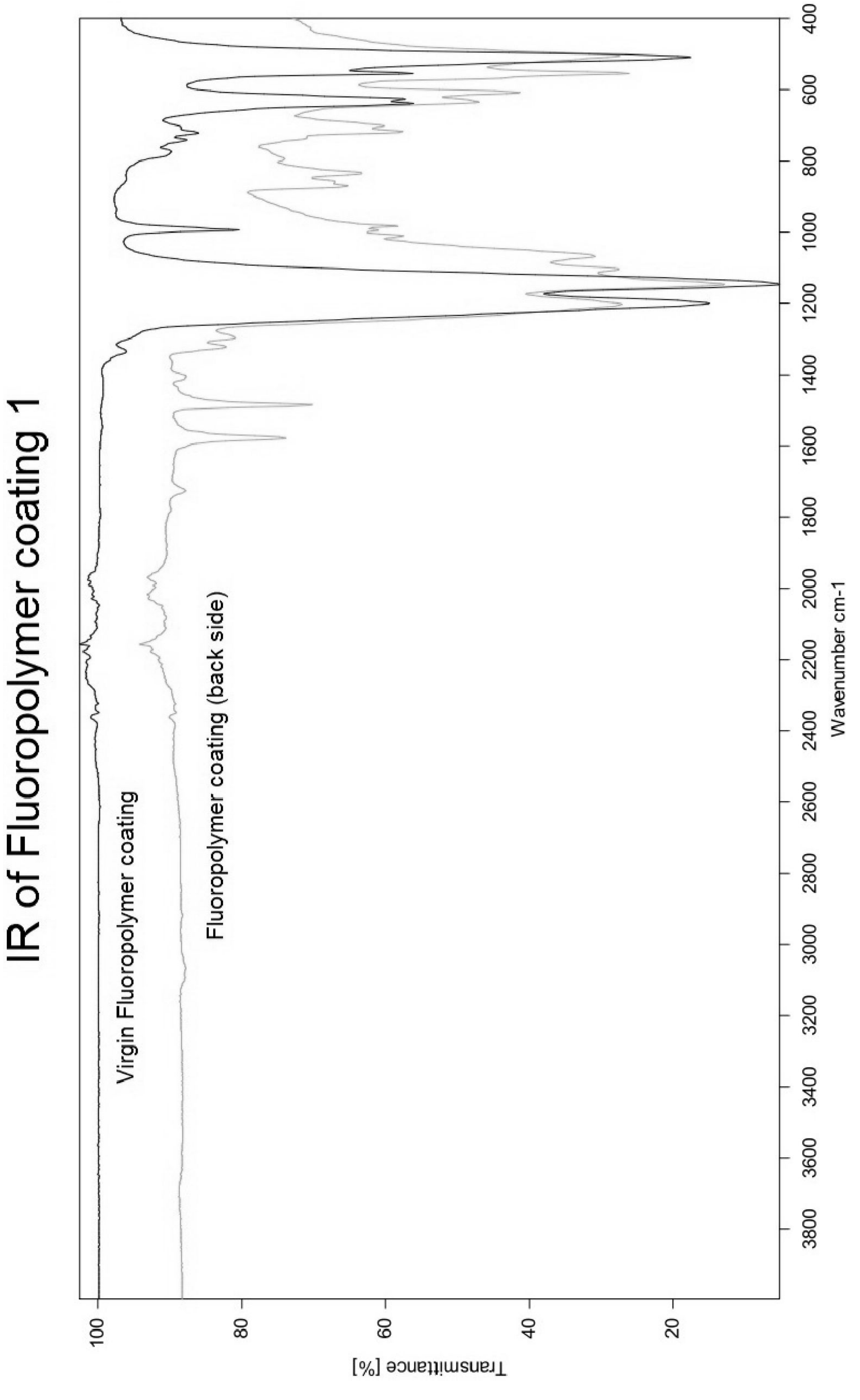
| | | | |
|---|---|---|---|
| Series Title | PE-HD and PE-mod extrusion | | |
| Extruder | | | |
| type | Cone Extruder | | |
| model | Conex 300-1 | | |
| Date | 5.9.2011 | | |
| Place | TUT Plastics and Elastomer Technology | | |
| | Nokiankatu 1, FI-38210 Vammala, Finland | | |
| Extrusion Material | | | |
| Extruder User | Juha-Pekka Pöyry | | |
| | | | |
| Die Coating | Hard Chrome Plating with Fluoropolymer | | |
| | | | |
| Throughput rate (kg/h) | 5 | 10 | 15 |
| | | | |
| Screw Speed (rpm) | | | |
| feeder screw | 13 | 26 | 40 |
| rotor screw | 7 | 7 | 7 |
| | | | |
| Temperature Profile (°C) | | | |
| Tg1 | 30 | 30 | 30 |
| Z5 | 125 | 125 | 125 |
| Z6 | 160 | 160 | 160 |
| Z7 | 125 | 125 | 125 |
| Z8 | 160 | 160 | 160 |
| Z13 | 170 | 170 | 170 |
| Z14 | 30 | 30 | 30 |
| Die | 230 | 230 | 230 |

# APPENDIX 4: PRESSURE DROP AND NORMAL FORCE DATA





# APPENDIX 5: IR CURVE OF FLUOROPOLYMER COATING 1



## APPENDIX 6: DSC COOLING CURVES