TAMPERE UNIVERSITY OF TECHNOLOGY

VILLE MYLLÄRI
PRODUCTION OF FILAMENT YARNS MADE OF PEEK
Master of Science Thesis

Examiners: Professor Pentti Järvelä, Professor Mikael Skrifvars, Dr. Seppo Syrjälä
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Abstract

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This project is a part of European commission collaborative Safeprotex project of Seventh Framework Programme to manufacture high protective clothing for complex emergency operations. The goal of this thesis is to manufacture polyetheretherketone, PEEK, fibers by melt spinning and modify them to provide antimicrobial, self-cleaning and antipollution properties.

PEEK has excellent thermal and mechanical properties and good chemical resistance. The literature review clearly shows that PEEK should be easily spinnable. Melt spinning is a process where polymer is melted, normally by extruder or piston system. The system of TUT is based on Göttfert capillary rheometer which is a piston system. Melt material is pushed through a small hole after which it faces cold air and starts to cool down. Solidified fiber is drawn to a roll.

PEEK modification is done by sulfonate groups that change the chemical structure so that functional properties are possible. Without modification the reaction does not happen. Reaction is based on benzophenone compounds that are excited by UV-light.

During the experimental part DSC, TGA and rheological tests were made to characterize PEEK. The results of these tests confirm that PEEK has excellent thermal properties and it should be easily spinnable. Fiber spinning of virgin PEEK turned out to be easy and the best achieved fibers were less than 20 μm in diameter. Operating temperature and hole diameter turned out to be the most important parameters in our spinning system. TUT piston system, Göttfert capillary rheometer is not designed for fiber spinning which lead to a few problems most importantly variations in fiber thickness.

PEEK modification was done by our Italian partner company Next Technology Tecnotessile. Modification provided wanted functional properties but it also made spinning more difficult, worsened thermal stability and made the fibers more brittle. Modified PEEK was mixed with virgin PEEK to avoid these problems. At best, 1.5 % of modified PEEK could be added to virgin PEEK and still be able to make fibers of it.

Tiivistelmä

TAMPEREEN TEKNILLINEN YLIOPISTO
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MYLLÄRI, VILLE: PEEK:n kuidutus
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Tämä diplomityö on osa Euroopan komission Seitsemännen puiteohjelman Safeprotex yhteistyöprojektia, jonka tavoitteena on valmistaa suojavaatetusta erityisen vaikeisiin pelastusoperaatioihin. Tämän diplomityön tavoitteena on valmistaa PEEK (polyeetterieetteriketoni) kuituja ja modifioida niitä siten, että niissä olisi funktionaalisia ominaisuuksia. Funktionaalisilla ominaisuuksilla tarkoitetaan tässä yhteydessä itsepuhdistuvuutta, bakteerien estokykyä ja saastuttamisen estokykyä.

PEEK:llä on erinomainen lämmönkesto, hyvät mekaaniset ominaisuudet ja hyvä kemikaalien kestokyky. Työn kirjallisuusselvitys osoittaa selkeästi, että PEEK:n pitäisi olla helposti kuidutettavissa. Sulakehruussa polymeeri sulatetaan, minkä jälkeen se puristetaan ohuen reiän läpi, normaalisti ekstruuderin tai mäntälaitteiston avulla. TTY:n laitteisto perustuu Göttfertin kapillaarireometriin, joka on mäntälaitteisto. Kohdatessaan kylmän ilman materiaali alkaa jäähtyä. Kiinteytynyt kuitu kelataan rullalle kelausmoottorin avulla.

PEEK:n modifiointi tapahtuu sulfonaattiryhmillä, jotka muokkaavat PEEK:n kemiallista rakennetta siten, että funktionaaliset ominaisuudet ovat mahdollisia. Ilman modifiointia PEEK:llä ei ole funktionaalisia ominaisuuksia. Funktionaaliset reaktiot perustuvat bentsofenoni-yhdisteisiin, jotka virittyvät UV-valon avulla.

Kokeellisen osan aikana PEEK:lle tehtiin DSC, TGA ja reologiset testit. Nämä testit vahvistavat, että PEEK:llä on erinomainen lämmönkesto ja että sen pitäisi olla hyvin kuidutettavissa. Modifioimattoman PEEK:n kuidutus osoittautui helpoksi ja parhaat saavutetut kuidut olivat halkaisijaltaan alle 20 μm. Prosessointilämpötila ja kapillaarin halkaisija osoittautuvat tärkeimmiksi kelausparametreiksi TTY:n laitteistossa. Göttfertin kapillaarireometri on rakenteellisesti suunniteltu viskositeettimittauksia varten, mikä kuituja kelattaessa johti tiettyihin ongelmiin. Pahin näistä ongelmista oli suuri vaihtelu kuitupaksuudessa, mikä heikensi prosessin stabiilisuutta.

PEEK:n modifioinnin suoritti projektin Italialainen yhteistyökumppani Next Technology Tecnotessile. Modifioinnin ansiosta sulfonoituun PEEK:in saatiin halutut funktionaaliset ominaisuudet, mutta valitettavasti kuidutettavuus ja lämmönkesto heikkenivät merkittävästi. Siinä missä neitseellinen PEEK on sitkeää, niin sulfonoitu on haurasta. Modifioitua PEEK:ä sekoitettiin neitseellisen PEEK:n kanssa, jotta nämä ongelmat pystyttäisiin välttämään. Parhaimmillaan 1.5 % sulfonoitua PEEK:ä pystyttiin sekoittamaan neitseelliseen PEEK:in ja vielä tämän jälkeen tekemään kuitua siitä.

Preface

The work during my Master of Thesis has been interesting and mind-opening. The amount of theoretical and experimental work has been in balance and I have been able to use things I have learned during the five years of my studies. Because this is a European commission collaborative project I have had a chance to improve my intercultural skills as well.

I want to thank my work instructors professor Pentti Järvelä, professor Mikael Skrifvars and Dr. Seppo Syrjälä for all the advices they gave me during this process. The Institute of Fibre Materials Science let me used their equipment during this work which I'm grateful for. People in Next Technology Tecnotessile provided us sulphonated PEEK and literature for chapter three which I'm grateful of. I want to thank Special laboratory technician Jyri Öhrling, and all the other people who taught me to how use the equipment or helped me in any way during this thesis.

I would also like to express my special gratitude to Aino whose support and encouragement was essential during all the hard work.

Tampere, 10.3.2011

Ville Mylläri

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Abbreviations, symbols and terms

ABS	Acrolynitrile butadiene styrene
BBIT	Butyl-benzisothiazolinone
BP	Benzophenone
BPK	Benzophenone ketyl
CNF	Carbon nanofiber
CNT	Carbon nanotube
DCOIT	4,5-di-chloro-isothiazolinone
DSC	Differential scanning calorimetry
ESIPT	Excited state intramolecular proton transfer
FDA	Food and Drug Administration
HDPE	High density polyethylene
IMHB	Intramolecular hydrogen bond
LCP	Liquid crystal polymer
OBMA	10,10’-oxybispheno arsine
OIT	n-octyl-isothiazolinone
NTT	Next Technology Tecnotessile
PA	Polyamide
PAI	Polyamide-imide
PAEK	Poly(aryl-ether-keton)
PBT	Poly(butylene terephtalate)
PC	Personal computer
PC	Polycarbonate
PE-HD	High density polyethylene
PEI	Polyether imide
PEEK	Polyetheretherketone
PES	Polyether sulfone
PET	Polyethylene terephtalate
PLC	Programmable logic controller
POM	Polyoxymethylene
PMMA	Polymethyl metacrylate
PP	Polypropylene
PPO	Poly(phenylene oxide)
PPS	Polyphenylene sulfide
PPSU	Polyphenylsulfone
PS	Polystyrene
PSU	Polysulfone

pyrithione	Mercaptopyridine-n-oxide
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
SEM	Scanning electron microscope
SPEEK	Sulfonated polyetheretherketone
TGA	Thermogravimetric analysis
TUT	Tampere University of Technology
Triclosan	Trichlorohydroxydiphenylether
UV-A	Ultraviolet radiation of wavelength 315-390 nm
UV-B	Ultraviolet radiation of wavelength 280-315 nm

A	Cross sectional area of the fiber
L	Length of the spinning path
Q	Mass throughput
R^2	Coefficient of determination
T_m	Melting temperature
T_∞	Temperature very far from the extruder
V_l	Speed of the fiber before the take-up device
V_0	Speed of the fiber after the spinneret
σ_s	Stress at the solidification point
Ø	Fiber diameter

Birefringence-index	Measure of orientation in anisotropic materials measured by the decomposition of a ray of light into two rays.
Compression-ratio	Extruders channel depth in the feeding zone divided by the depth in the metering zone.
DDR, Draw down-ratio	Fiber speed V_l near the take-up device divided by the fiber speed v_0 near the spinneret.
Die swell ratio	The ratio of maximum polymer diameter after the spinneret and the diameter of channel.
L/D-ratio	Ratio of extruders screw length and diameter
Take-up velocity	The velocity of the fiber near the take-up device.

1. Introduction

This Master of Science thesis about PEEK melt spinning is a part of collaborative Safeprotex-project. The funding for this project comes from European Union and this project belongs to the Seventh Framework Programme (FP7) for research and technological development. Safeprotex project tries to manufacture clothing for complex emergency operations thus reducing the risk of injury in complex system. Inside this project there are several smaller projects and 19 participants from nine different countries. TUT's part of the project is to manufacture fibers first from unmodified PEEK and later from modified PEEK provided by one of our collaborative partners. [72]

Polyetheretherketone, PEEK, is a thermoplastic with a great potential. Although rarely used because of its price PEEK has managed to stabilize its position in high temperature applications [1]. In this project TUT's goal is to make fibers from PEEK and modify it so that the fibers could provide antimicrobial, antipollution and self-cleaning properties. These fibers could be then used in high-protective clothing.

This work consists of literature review and experimental part. In the literature part PEEK's properties, manufacturers and additives will be reviewed. Melt spinning processes can be based on extruder or piston and the characteristics of both will be listed. In melt spinning process polymer is melted and pushed through a hole. Fiber cools down, solidifies and then it is drawn to a roll. The most important processing parameters are operation temperature, hole diameter, length of the spinning path, mass throughput, take-up velocity and cooling conditions [23]. These parameters will be reviewed first theoretically and then in the experimental part.

Melt spinning of PEEK is not a new invention. In fact it has been done since the 1980s and nowadays there are at least two commercial manufacturers of PEEK fibers [37, 38]. The goal of this project is to go a little further: create very thin fibers and modify PEEK so that the fibers would provide functional properties. Theoretically addition of sulfonate groups to PEEK should provide functional properties. The reaction is based on benzophenone ketyl radical formation. First benzophenone gets excited with UV-light and then it abstracts hydrogen from a functional group. This radical has a long lifetime and it should theoretically decompose organic materials. [61] The goal of this project is to find out is this really the case and also how modification affects mechanical properties or spinnability.

Experimental part consists of PEEK characterization with DSC, TGA and rheological tests. As a result of these tests one grade, Victrex PEEK 151G, is selected for further testing. This grade is used to find the limits of spinnability of unmodified PEEK. Our test system is based on Göttfert capillary rheometer which has some limitations but is capable of melt spinning. When manufacturing very thin fibers all the parts of the process has to be in balance. Mass throughput has to be stable and very small. Cooling conditions have to be optimal and winding system steady. Variations in the process should be minimized to improve quality. Despite of the equipment limitations, the goal is to optimize system parameters in this process. The mechanical properties of unmodified filaments are tested. SEM is used to examine the surface quality and optical microscope to calculate the fiber thickness and deviation. In addition, a thermal imaging camera will be used to see the behavior of the fibers.

PEEK modification is done by our Italian partner company Next Technology Tecnotessile. The goal is to mix this grade with virgin PEEK, test the fiber spinning process, find the maximum sulfonated PEEK concentration and test the manufactured filaments. Previous tests have shown that benzophenone compounds should give functional properties to polymers but they also worsen the mechanical and thermal properties [55, 58]. A compromise between the mechanical and functional (antibacterial) properties should be thus found.

Overall the concept is promising. If PEEK could be modified to provide functional properties without the loss of mechanical properties it could lead to useful real-world applications.

2. PEEK melt spinning feasibility study

2.1. PEEK generally

2.1.1. Properties

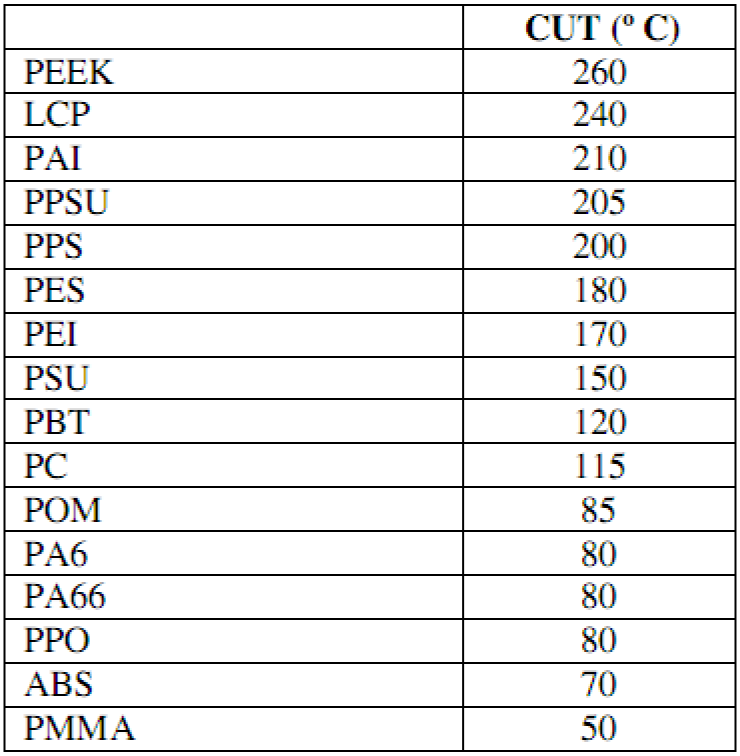
PEEK (polyetheretherketone or poly(oxy- 1,4-phenyleneoxy- 1,4-phenylenecarbonyl- 1,4-phenylene)) is a rather expensive, semi-crystalline thermoplastic with many outstanding properties. It has a very high working temperature up to 260 °C, excellent chemical resistance to most solvents and good mechanical properties. Water absorption and flammability are low, radiation resistance good and electrical properties good. In dynamic fatigue tests 10^7 cycles decrease its tensile strength only 10 % and also the resistance to abrasion is very good. PEEK can be processed on all conventional processing techniques. The only problem is the high processing temperature which may require modifications to equipment. PEEK is approved by FDA, Food and Drug Administration. More about general, mechanical and thermal properties of PEEK have been summarized in Appendix 1. [1-6]

Table 2.1. *Properties comparison of four different thermoplastics. [2-4]*

	PEEK	**PE-HD**	**Nylon 66 ® (PA 66)**	**Nomex ® (aromatic PA)**
Density [g/cm^3]	1,32	0,93	1,21	1,33
Tensile strength [MPa]	100	25	80	37
Young's modulus [GPa]	3,6	1,1	2	0,8
Elongation at break [%]	50	500	50	28
Melting point [°C]	343	130	263	400
Glass transition temperature [°C]	146	-120	50	272
Max. working temperature [°C]	260	90	85	200
Price [EUR/kg]	80	2	3	40 (spunlace)

There is some comparison between a few common thermoplastics in Table 2.1 so that it is easier to understand why fibers of PEEK would be so desirable. Polyethylene and Nylon are probably known for most. Nylon and Nomex are both polyamides and trademarks of DuPont. The difference between these two is that Nomex has aromatic rings in its backbone and therefore it has better mechanical and thermal properties than Nylon. Nomex is commonly used in firefighter's suits so comparison helps to determinate whether PEEK could replace Nomex someday. It is easy to notice that PEEK has even higher maximum working temperature. Although Nomex have fairly good chemical resistance PEEK has even better. PEEK can stand acids and alkalis better than Nomex. Mechanical properties are much better when using PEEK. More about continuous use temperatures can be found in Table 2.2. [2-4, 7]

Table 2.2. *Continuous use temperatures of some high performance plastics. [1]*



	CUT (° C)
PEEK	260
LCP	240
PAI	210
PPSU	205
PPS	200
PES	180
PEI	170
PSU	150
PBT	120
PC	115
POM	85
PA6	80
PA66	80
PPO	80
ABS	70
PMMA	50

PEEK is not the only member of the poly(aryl-ether-ketone), PAEK, family. There are many other members like PEK, PEKK, PEEKK, PEEEK, PEKEKK, PEKEKEEK and PEEKEK (E stands for ether and K for ketone). However, PEEK is the only one currently having commercial significance. All of these materials have excellent thermal properties. Melting point rises when ketone/ether- ratio is increased [10]. PEEEK has the lowest melting point of 324 °C and PEKK the highest 386 °C. Blends of PEEK and PEK have been tested successfully. It was noticed that these two relatives have good adhesion and that addition of PEK to PEEK improved mechanical properties. [8-11]

2.1.2. Manufacturing

Many of these properties, especially good thermal resistance, are a result of aromatic rings in the polymer chain. PEEK can be made by two general routes: by nucleophilic or by electrophilic polycondensation. The first is the reaction of potassium salt of hydroquione with 4.4’-difluorobenzophenone in a high boiling solvent, diphenyl sulfone, at temperatures close to the melting point of the polymer (343 °C). Polymers made by nucleophilic reaction are claimed to be useful especially for wire coating. In the second reaction type, electrophilic process, formation of the carboxyl link is made by polyaroylation in a liquid HF with e.g. BF_3 catalysts. The reaction is also possible in solvents such as dichlorobenzene with an excess of $AlCl_3$. The reaction is carried out at temperatures close to room temperature or even below it and it normally produces polymers with low molar mass. Capping agents such as 4-chlorobiphenyl or 4-phenoxybenzophenone are used to control the molecular weight, branching and gel formation during polymerization. Electrophilically processed PEEK has normally high degree of branching and therefore lower melting point than normally. The main difficulty in both of these reactions is to keep the crystallisable polymer in solution. The chemical structure of PEEK is demonstrated in Figure 2.1. [1, 5, 6]

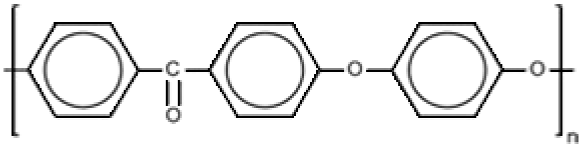


Figure 2.1. *The structure of PEEK.*

2.1.3. Suppliers and use

The annual production of PEEK is about 1,300 tons (2002) and the leading supplier is currently Victrex. Normally PEEK is used in applications that require good thermal stability, water and wearing resistance and electrical properties. During the last few years especially injection molded applications have become more popular. Relatively high price limits its use in demanding applications such as metal replacement. Key markets are aerospace, transportation, industrial, electronics and the food processing industry. Some products made of PEEK are listed in Table 2.3 [1]

Table 2.3. *Some products made of PEEK. [1, 12]*

Sector	**Consumption [tons/year]**	**Use examples**
Automotive	500	Piston units, seals, washers and bearings
Electrical	300	Electrical insulator, connector jacks, potentiometers, under sea environment control equipment
Consumer	<< 50	High-tech speakers
Industrial	300	Food contact applications, metal replacements, boiler pins, steam faucets, industrial coffee machines, regenerative pumps
Other	200	Medical devices, dental instruments, endoscopes, haemodialysers

It is easy to notice that automotive industry is the biggest market sector with about a 40% share and consumer products are rarely made of PEEK because of its price.

2.2. PEEK additives

PEEK is one of the most expensive thermoplastics with excellent properties. So it is natural that additives used with it are for improving properties, not for making it cheap. Because of these naturally good properties PEEK does not even need that much additives. Processibility of PEEK is typically good, but only if melt stabilizers have been used. Unstabilized PEEK shows a strong tendency to crosslink which is highly undesirable because melt viscosity rises and mechanical properties become weaker. Metal oxides (e.g. zinc oxide) or sulfides (e.g. zinc sulfide) are good stabilizers for PEEK. Also organic aromatic phosphite and diphosponite are used as stabilizers. The first one is more efficient of these two and it has to be mentioned that oxalic acid is recommended conjunction with these two to improve melt flow. [6, 13]

Reinforcing materials and fillers are the second common type of additives used with PEEK. PEEK / carbon fiber or PEEK / glass fiber are both well studied composites. Hydroxyapatite, aluminum oxide and aluminum nitride (micro-size) are typical fillers but nowadays the focus is definitely towards nano-particles. Nano-particles improve mechanical properties even in small amounts. Nano-size aluminum oxide and aluminum nitride improve microhardness of PEEK much more than micro-size versions of these additives [14]. PEEK has naturally very good wear resistance but compounding with nanometer size Si_3N_4 improves even more its tribological properties. Naturally PEEK has a dynamic friction ratio of 0.25 but with 15 % (wt.) of nano-size Si_3N_4 it can be lowered down to 0.15 [15, p.85]. Also nanometer ZrO_2 improves the wear properties according to Wang's tests [16]. The lowest wear rate was obtained at 7.5 % (wt.) of ZrO_2 added which reduced the wear rate 46 % compared with unfilled PEEK. [6, 17]

Carbon nano tubes (CNT) and carbon nano fibers (CNF) are added to PEEK to improve tensile properties and also wear resistance. They do not have any significant effect on melting point or crystallinity but tensile strength improves from less than 100 to over 120 MPa and also modulus grows notably. Addition of CNT or CNF also improves wear and friction properties the same way as Si_3N_4, ZrO_2, AlN or Al_2O_3 does. [17, 18]

PEEK is inherently flame-retardant and therefore any additional flame retardants are not needed [9]. Normally unfilled PEEK has a light brownish color. Often that is not the most wanted or attractive color and therefore new colorants have been developed. PEEK is a difficult thermoplastic to color because it has so high processing temperatures and because the inherent color is difficult. PEEK can be colored with fluorescent dyes [19], color and additive concentrates [20], or with polyimide based inks [20]. About a ten different colors are available. For many products made of PEEK the coloring is however irrelevant and therefore colorants will not be reviewed more precisely. [5, 13, 21]

2.3. Technical procedure and equipment

2.3.1. Melt spinning process generally

Melt spinning is a process where melt polymer passes through a spinneret, solidifies rapidly and forms a fiber structure. The polymer has to be melted and preferably mixed which is normally done with a screw extruder. It is also possible to use piston systems but the lack of mixing may cause problems. Extruder is normally used in commercial applications because it ensures sufficient throughput. After melting granulates, the mass goes through a hole or multiple holes. The spinneret is a device very similar to a bathroom shower head purpose of which is to divide melt polymer into smaller holes. The number of holes can vary from one to many hundreds. After the spinneret the filament is drawn by the wind-up unit at constant take up speed. Right after the spinneret the polymer faces cold air and starts to cool down. The filament should be totally solidified before touching the first take-up unit or otherwise the process will fail. A typical melt spinning machine can be seen in Table 2.2. [22, 23, 24]

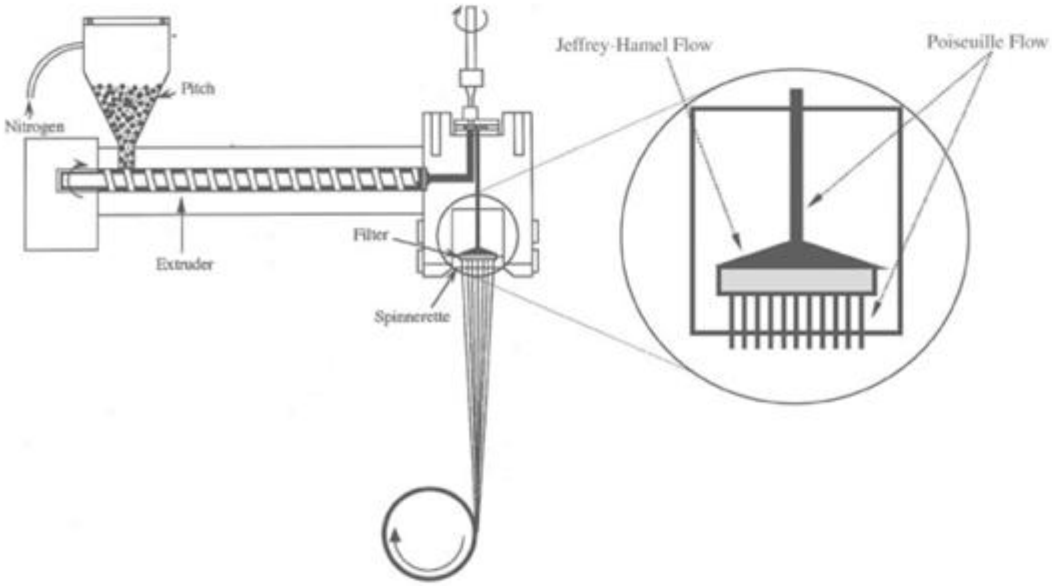


Figure 2.2. *A typical melt spinning machine with a screw extruder. [26]*

Granulates should be dried before they are melted. This is important because too much water within the polymer can ruin the process. The allowed moisture concentration depends on the polymer and can be as small as 0.005% for PET, polyethelyneterephthalate. PEEK pellets have relatively small water absorption of 0.5% but they should be dried as well to less than 0.02% water concentration to ensure the best possible quality. Required drying times are 2 h in 160 °C, 3 h in 150 °C or overnight in 120 °C for PEEK [25].

2.3.2. Screw extruder

In majority of commercial processes melting is done by continuous screw extruders. While the screw rotates, it heats, homogenizes and transports the material forward. Screw extruders have three zones: feeding, compression and metering. The goal is to make the material as homogenous as possible in a right temperature. Material is fed through a hopper and generally it flows by gravity to the extruder barrel which is annular space between the barrel and the screw. Polymer is heated with frictional and conduction heat. When polymer is moving forward friction between it and the metal barrel generates substantial amount of heat. The rest of the heat needed comes from barrel heaters by conduction. At the end of the screw, in the metering zone, polymer should be totally melted and homogenous. Two typical single screws and their section lengths for Victrex PEEK processing are shown in Figure 2.3. [25, 27]

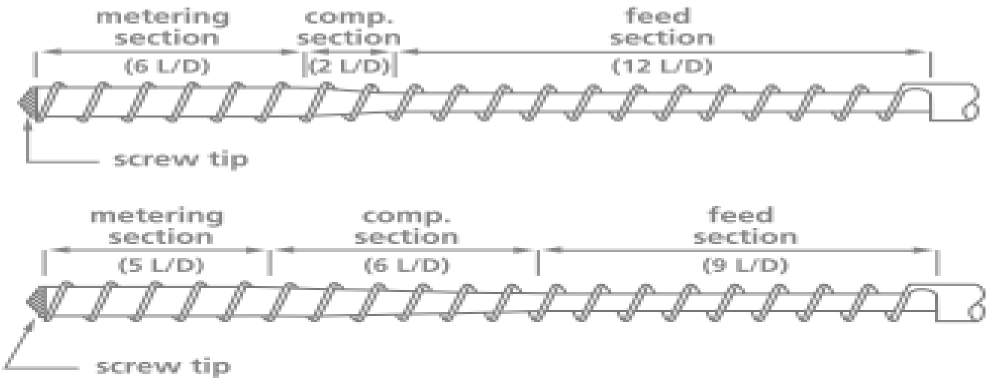


Figure 2.3. *Two typical screws for processing Victrex PEEK. [25]*

Victrex recommends L/D-ratio (L meaning channel length, D diameter) to be something between 16-24 and compression ratio (channel depth in the feed section divided by channel depth in the metering section) between 2-3. Screws in Figure 2.3 have very different compression section lengths but this is not a problem as long as feeding section is long enough. Extruder should be capable of reaching and maintaining continuous 400 °C temperature. Therefore cast aluminum heaters are not suitable and should be replaced with alloy or ceramic heaters. Barrel capacity should be matched with output so that residence time is as small as possible. Processing of PEEK is possible with all the normal screw designs except PVC-type screw which has too short feeding section. [25]

The quality of the polymer is very important when making fine filaments. There should be no impurities or air bubbles because they can lead to filament breakages. To ensure these goals there is a filter before the spinneret which removes these impurities. This filter is normally fine sand of alumina held in place by metal screen. Before the spinneret and the filter there is a pump so that the flow of polymer would be constant. This metering pump controls and maintains the flow because any interruptions would break the filament or weaken their quality. Spinnerets are normally 3-30 mm thick and made of stainless steel or other suitable material. Corrosion resistance is very important and spinnerets should be easy to machine. The spinneret has a certain amount of orifices which can be arranged in many ways e.g. concentric circles, parallel rows and scatter patters. In commercial applications it is desirable to have many holes and therefore many filaments but cooling among other things may restrict the number of the holes. Holes should have the same diameter for obvious reasons. To avoid the breaking of the filaments, cleaning of the holes should be done regularly. Also the design of spinneret is important so that it will not have any dead zones that could affect the homogeneity of the polymer mass. [8, 28, 29]

2.3.3. Piston extruder

Instead of extruders it is also possible to use piston systems to melt the polymer and push it through a hole. One example of this kind of system is the Göttfert capillary rheometer (Reograph 6000) used during the experimental part of this work. Piston systems are mostly for small-scale experimental work. Piston system is optimal when making fine or ultrafine filaments because of its low throughput possibility [22]. There are only a few basic components in piston extruder and also operation is fairly simple. Polymer material is charged into the barrel. Hydraulic piston presses the material through a die. Pressure is generated by a hydraulic system. For example Reograph 6000 can generate a thrust of 60 kN and withstand a maximum pressure of 200 MPa [30]. Polymer must be totally melted before entering the die and therefore there are heaters around the bore. The difference to a screw extruder is the lack of mixing that may cause quality problems. The process is controlled by the control-unit which can be based on PLC (programmable logic controller), PC (personal computer) or microprocessor. A modern piston extruder includes sensors for temperatures, pressures and piston movements. For example Rheograph 6000 has only a few buttons in the base frame and mostly it is controlled and monitored by PC. [31, 32]

2.3.4. Quenching

After the spinneret filament starts to cool down. Take-up rolls are horizontally below the spinneret and before the filament touches them the material should be totally solidified. At first, the filaments were cooled only by natural convection but it was really slow and required a long cooling distances. Du Pont discovered in 1939 that cross flow of air would reduce the distance from 6 m to 1.5 m. Since that time new developments have been made and the cooling time has been managed to reduce to 0.05 s for fine yarns. Three common cooling methods in use are: cross-flow quench, in-flow quench and out-flow quench. Cross-flow quench is used for fine and large filaments and for spin packs. In-flow quench chamber requires annular hole-pattern. The air penetrates the hollow bundle and flows down within the bundle cooling it down simultaneously. The out-flow quench system is also for ring-shaped spinnerets. The air is coming above the spinneret to the hollow tube of filaments and then penetrating through it and cooling it down at the same time. Out-flow quenching is used for filaments with high deniers. [8, 28]

2.3.5. Take-up

After the spinneret the fibers must be drawn and that is done by take-up machines. Modern take-up machines include not only a winding unit but also yarn guiding, yarn cutting, aspirators, godets (rotating rolls that transport, stretch or thermally treat yarns), heating system and different kind of sensors. Hundreds of variations have been developed for different purposes. Take-up speed has risen from less than 1500 m/min to up to 9000 m/min. Friction drives is the most common type but also tension-controlled and surface speed controlled machines have been made. Improved controlling, new godet systems and new configurations have made it possible to increase take-up speeds radically. Godets have normally a diameter of 75-300 mm and they can be supplied with internal resistance or induction heaters. Take-up machine can also include separator rolls that are meant for changing the direction of the yarn. [8, 28]

2.4. Processing parameters

There are a few general parameters that have effect on the process in addition to the material. These are extrusion temperature, dimensions and number of spinneret holes, mass throughput, length of the spinning path, take-up velocity and cooling conditions. Different materials have different properties and processing conditions. These processing parameters will be reviewed in a general level and also considering the special properties of PEEK. [23]

2.4.1. Operating temperature

Operating temperature depends on the melting point and is normally 20-60 °C higher than T_m with PEEK and 60-90 °C higher when using e.g. polypropylene. If the polymer starts to degrade close to the melting point it cannot be used in melt spinning. This is not a problem with PEEK but not all the extruders can handle the extreme temperatures needed. PEEK has a normal operating temperature of 360-400 °C in melt spinning. Raising the temperature decreases viscosity but if the temperature is too high the polymer starts to degrade. [2, 4, 25, 28, 33]

Fourné [8] first suggested in 1995 that increasing the temperature would improve the quality of the melt spinning process of fine filaments. This was also the case in Golzar’s tests [33, p.109]. He found out that increasing the melt temperature from 385 to 400 °C reduced spinning line breakages and improved the stability of time-dependent variables. Stress in the solidification point decreased from 13.5 to 9 MPa and the maximum velocity gradient from 523 1/s to 407 1/s. It has to be noted that during these test the lower temperature was 370 °C (not 385 °C) and it was taken from a theoretical PEEK fiber formation model. [33]

2.4.2. Dimensions and number of spinneret holes

Spinneret contains varying number of holes that have the same dimensions. Normally the holes are round but it is also possible to make non-circular holes. This, however, is not relevant considering the goal of this study. When choosing the right number of holes, one has to know the limitations of the extruder capacity, cooling systems and take-up lines. In commercial systems more filaments means more money if the process allows it. But when the number of filaments increases it will be more difficult to cool down them evenly. Different kinds of quenching systems were listed in the previous chapter. Special kind of spinnerets can contain up to 200 000 holes but a typical number is roughly a hundred. The spinneret diameter is normally 100-500 μm but it can be even smaller or bigger. For high pressures the plate thickness is 8-25 mm, for low pressures it can be as low as 0.2 mm. L/D-ratios are normally 1-20 and the smaller the hole diameter is the smaller the L/D-ratio. More about screw parameters for PEEK has been described in chapter 2.3.2. [8, 28]

Extrudate (die) swell has been known for long in the polymer industry. After the die the polymer mass swells because of the relaxation processes in the spinneret channel. It is important to minimize the die swell because it weakens the quality of the fibers by making them more irregular. Increasing the temperature helps but also L/D-ratio is important. Experiments [24, p.87] have shown that the die swell- ratio (the ratio of maximum polymer diameter after the spinneret and the diameter of channel) decreases when the L/D-ratio increases. This should be taken into consideration when choosing the spinneret. [8, 23, 24]

Making ultra-fine filaments requires the mass throughput to be very small. Increasing the number of spinneret holes allows altering the throughput per filament easily. Golzar [33, p. 114] tested the limits of spinnability by changing the mass throughput and diameter of the holes. Bigger diameter made it possible to use bigger draw down ratios but it did not have much effect on the take up speeds. Repkin [34] studied the connection between spinneret holes and spinning failures and found out that increasing the diameter improved the quality of the process and decreased the number of failures.

2.4.3. Mass throughput

Mass throughput can vary in a wide range depending on the equipment used. When using spinneret with multiple holes the total mass has to be divided by the number of holes to get the mass per one filament. Ziabicki [23, p. 151] has stated the equation of continuity which has to happen in the process or otherwise the filament will break:

$$AV_l\rho=Q=\text{constant} \qquad (1)$$

Where A is the cross sectional area of the fiber, V_l is the take-up velocity, ρ is the density of the polymer and Q is the mass throughput. If the fiber diameter is 20 μm, take-up velocity 2000 m/min and the spinneret contains 50 holes, the mass throughput is then 30 g/min. Problems may arise if the number of holes or fiber diameter is small. Biggest extruders have the melting capacity up to 30 kg/min but most of them will most likely have too big minimum mass throughput and therefore some kind of piston systems has to be used to get very thin filaments. [22, 23, 28, 33]

With piston system as low as 15 mg/min (0.1 dtex) PEEK fibers has been manufactured [22, p.2152]. Golzar's [33, p.104-106] tests show that increasing the mass throughput allows bigger take-up velocities. Decreasing the throughput increases the stress and strain rate which leads to breakages because it cannot be controlled by the structure formation of the polymer. The failure mechanism of the fiber is related to the mass throughput. In very low throughputs (<0.5 g/min) the ductile failure was estimated to be the most probable reason for failures. For higher than 1.0 g/min throughput brittle fracture takes place. [33]

Increasing the mass throughput obviously makes the cooling path longer because the fiber has to solidify. There are two easy ways to determine the point where the fiber has become solid: from the speed profile (the first point along the spinning line where fibers speed equals take-up speed) or from temperature distribution (temperature reaches glass transition temperature). Golzar [33, p.97] found a good relation ($R^2=0.983$, R^2 being the coefficient of determination) between solidification path and throughput for PEEK

$$L\approx 26Q+6.4 \qquad (2)$$

Where L is the length of the spinning path in cm and Q is throughput in g/min. The test was carried out in different take-up speeds and it was noticed that it had very little effect on the spinning path. [33]

2.4.4. Length of the spinning path

Length of the spinning way is typically 2-5 m totally in commercial spinning lines. The length to the take-up point should be at least long enough for the fiber to cool down and solidify. This depends of course on the material, cooling conditions, and extrusion temperature. At average spinning conditions the filament temperature reaches T_∞+30 °C (T_∞ is the temperature very far from the extruder) at a distance of 30-100 cm from the spinneret. The longer the distance is, the bigger is the take-up tension. This is due to the increased air friction. [23]

Golzar [33, p.111-112] studied the effect of running length on the fiber speed and velocity gradients. He found out that for a long running length the fiber speed increases in two steps. The first happens through a conventional thinning process of melt spinning and the second because of plastic or elastic deformation. The second step is a result of increased air resistance which leads to thinner fibers according to equation (1). Long spinning path also increases the stress at the solidification point and the maximum velocity gradient of fibers. Minimum and maximum values for the length of the spinning path are relative easy to understand. The minimum is related to the cooling conditions and the point of solidification. The maximum length is stress related. Because stress increases almost linearly as a function of spinning length due to air resistance, at some point the filaments will break [23, p. 186]. This value was defined as a limit of fiber tensile stress along the spinning line and it is normally $0.5\text{-}0.67 \cdot \sigma_s$ (σ_s being the stress at the solidification point). It was also noted that when making fine or ultra-fine PEEK filaments it was better to use short spinning path. [33]

2.4.5. Take-up velocity and draw down-ratio

Take-up velocity is normally from a few hundred to a few thousand meters per minute in a gaseous intermediary. Tendency has been towards higher take-up velocities and nowadays velocities up to almost 10 000 m/min are possible. It is easy to understand that constant throughput and increased take-up speed means thinner fibers (equation 1). Golzar [33, p.60] tested the connection between take-up speed and elongation at break and noticed that at the same take-up speed bigger mass throughput increased the elongation at break. Bigger throughputs also made it possible to use bigger take-up speeds. Increase in take-up speed leads to an almost linear increase in take-up tension [23, p.184]. Golzar [33, p.113] summarizes that fine fibers can be spun under relatively high take-up speeds. Birefringence-index, which tells the amount of orientation in the line, increases rapidly along with the increased take-up speed. [8, 28, 33]

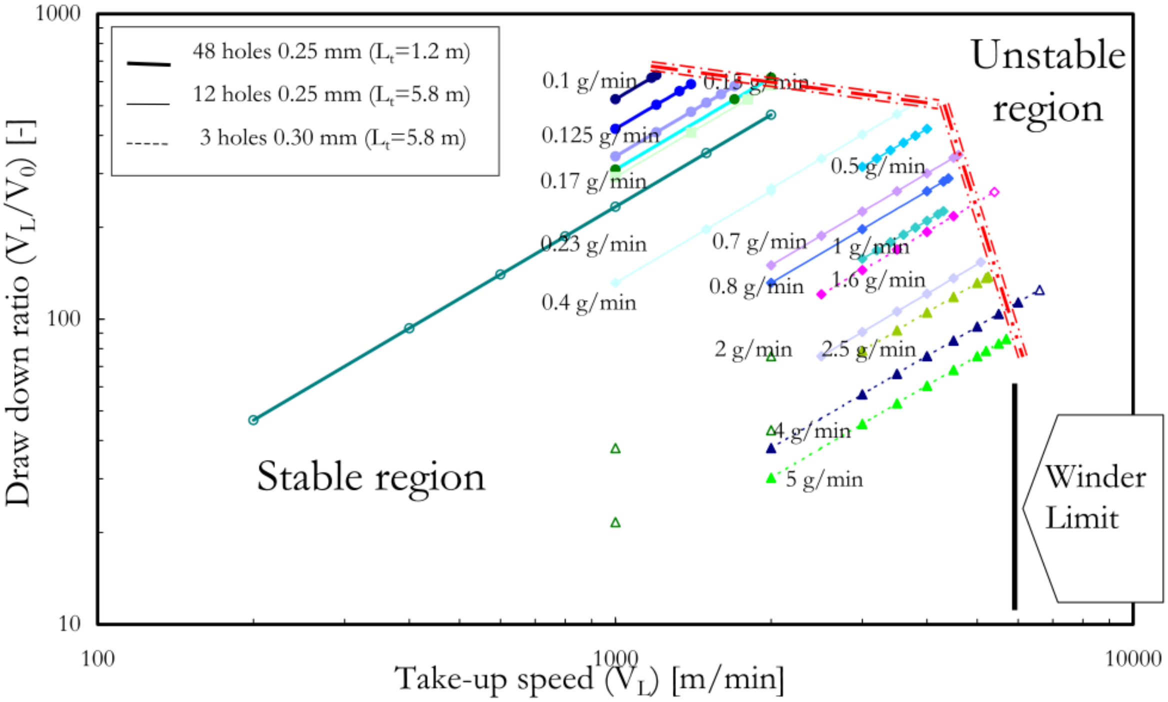


Figure 2.4. *Stable and unstable regions of PEEK with different parameters. [33, p.106]*

Draw down-ratio is not independent variable but it can be calculated from the mass throughput and take-up speed. It is defined as V_L/V_0 where V_L is the take-up speed and V_0 is the initial speed. For PEEK, draw down-ratios up to near a thousand have been tested successfully. Golzar (Figure 2.4) made a graph of stable and unstable regions in different take-up speeds, mass throughputs and draw down ratios. From the graph it is easy to notice that biggest draw down ratios are possible to get at a relatively low take-up speeds and small throughputs. However getting the draw down ratio as high as possible is not the main goal but rather finding the optimal take-up speed for a small throughput. Increased draw down ratio, as well as improved take-up speed, improves tenacity [nN/dtex] but the improvement is rather small however. [33, 28]

2.4.6. Cooling conditions

After a filament passes through a spinneret it starts to cool down. Most systems have a quenching cabinet to reduce the length needed for cooling. Fourne [8 p.347-367] has made an extensive research about different quenching systems and their parameters. Normally air velocity is about 1 m/s but it varies a lot depending on the system. The size of the quenching cabinet should be right so that the filaments cool down efficiently and evenly. High air velocities create turbulence which is not desirable under normal circumstances. Filaments may cool down unevenly or even be damaged under turbulent conditions. [8]

As simplified, the goal is to create steady cooling conditions. However, it is possible to use heating tube right after the spinneret. The idea of a heating tube is that the filament cools down slowly in the beginning or that there is a hot zone between the quenching areas. Increased temperature decreases viscosity which decreases stress in the spinning line. However, according to Golzar's test [33, p.110] the heating tube did not affect the fiber speed and it did not improve the stability of the spinning process. [33, 35]

Several tests have been made about the cooling rate and its effects on density and crystallinity. White [24, p.116] did not find any connection between cooling rate and crystallinity with PET and polyamide fibers. Also density was constant at different cooling rates. However birefringence-index, which is a measure of overall orientation, increased dramatically when cooling rate increased. Golzar [33, p. 87] made tests with PEEK and tried to find out how mass throughput and take-up speed affect cooling times. Doubling the take-up speed increased the cooling time only a little. The same outcome happened when increasing the mass throughput. So according to the tests creating thick fibers at high speeds requires longest cooling distances. [24, 33]

2.5. Commercial producers of PEEK fibers

There are not many commercial producers of unreinforced PEEK fibers. Even the number of PEEK bulk material manufacturers is limited because PEEK has relatively low volumes and high price. Ides – the plastics web page [36] has listed about 25 companies that have something to do with PEEK:

Table 2.3. *Companies that make or refine PEEK. [36]*

Victrex plc	Lubrizol Advanced Materials	CoorsTek
Devol® Engineering Polymers	PolyOne Corporation	Ensinger Inc.
Solvay advanced polymers	TP Composites, Inc.	Infinity Compounding Corp.
Kern GmbH	LATI S.p.A.	LEIS Polytechnik - polymere
SABIC Innovative Plastics	Lehmann & Voss & Co.	Saint Gobain Performance
Invibio Inc.	Ovation Polymers Inc.	Greene, Tweed & Co.
Quadrant Engineering Plastic Products	RTP Company	Zeus inc.
EPIC Polymers Ltd.	Nytef Plastics, Ltd.	Evonik Degussa AG
Asia International Enterprise	Witcom Engineering Plastics	Zyex

In addition to these companies, there may be a few extra companies that have not been listed in Ides web page. These listed companies may have different market areas and where one of them may do only bulk material other may have specialized in composites. Victrex is currently the leading manufacturer of bulk PEEK but it does not make fibers. There are at least two companies that have specialized in manufacturing thin PEEK fibers commercially. Zeus announced at the beginning of 2009 that it had started the production of drawn PEEK fibers. The diameter of the fibers varies between 0.07-1.0 mm and they are available at different colors. Currently PEEK products are custom orders only. The other company and trade mark is Zyex which is best known for its production of tennis strings. It has been testing PEEK fiber spinning since the 80's being one of the pioneers of the industry. According to Zyex, it is now the leading producer of PEEK fibers which is not hard to believe considering the limited market sector. It products monofilaments at diameters between 0.07-2 mm and multifilaments from sizes (decitex) 75 to 550 and filament number between 15-30. Like Zeus, also Zyex offers products in different colors. Zyex is also developing new special products made of PEEK like hollow monofilaments, short cut fibers and fine rods and tubes. [25, 36, 37, 38]

2.6. Properties of melt spun PEEK

As learned in the previous chapters there are only a few PEEK fiber manufacturers and also small-scale testing has been limited. As a result, there is a limited amount of data available of the properties of melt spun PEEK. In most cases it is not enough that PEEK *can* be spun. It should have good mechanical properties as well. Golzar [33, p.65] studied the effect of take-up speed and draw down ratio to the elastic modulus of spun filaments. Modulus was strongly dependent on the mass throughput and draw down ratio. At high throughput and small ratio modulus was about 1 GPa but with small throughputs and high ratios (~500) it rose to 5 GPa. This is caused by orientation process which happens at higher draw-down ratios. Also stress-strain curves were made. Tensile strength of the filament was tested to be about 600 MPa at best. This is approximately six times higher than the value of less-oriented PEEK. Tests with oriented polyethylene fibers have shown that this result is plausible [64]. At higher take-up velocities the tensile strength did not improve, maybe even decreased a little. Instead, elongation at break dropped significantly at higher take up speeds. Smaller throughputs improved tensile strength and made elongation at break smaller. [33]

Zeus, manufacturer of PEEK fibers, announces the properties of its fibers in the web page. Minimum tensile strength for 70 μm fibers is about 1.7 kg which is similar to about 330 MPa**.** Elongation at break is 18-35% and shrinkage 2-6%. [37]

PEEK has normally molecular weight of around 30 000 g/mol. Because the molecular weight of one unit is almost 300 g/mol this leads to about hundred repeat units. This is very small number compared with an example polyethylene which can have tens of thousands repeat units. Yuan and team [71] tested the effect of molecular weight on PEEK properties. Shear viscosity difference between 80 (PEEK80) and 129 units (PEEK129) is over a decade at low shear rates. Bigger molecular weight increases shear viscosity. Tensile strength at yield of these two grades is fairly similar but elongation at break is over twice as big with PEEK129 (28 vs. 64 %). Also tensile strength at break is bigger with PEEK129 (70 vs. 90 MPa). Modulus is not dependent on the molecular weight but impact strength improves with higher molecular weight. Low molecular weight PEEK80 has the highest melting temperature and crystallinity. Yuan concludes that molecular weight has significant impact on PEEK's properties. For melt spun fibers this should also be the case. This means that both material and processing conditions have effect on the properties of melt spun PEEK.

3. Theory of PEEK modification

Very little literature was found about modification of PEEK for antibacterial/antipollution/self-cleaning purposes and therefore alternative materials were used as an example in this chapter.

3.1. Basics of photochemistry

It is impossible to understand how functional additives for antimicrobial, self-cleaning and antipollution purposes work without knowing the basics of photochemistry. The Sun is obviously the most important source of light. Harnessing the solar energy is important because it provides cost and pollution free energy source. Earth’s atmosphere blocks some of the electromagnetic radiation and therefore wavelengths from only approximately 295 to 2500 nm reach Earth’s atmosphere. Higher-energetic part of the UV-B radiation (280-295 nm) is filtered off by the stratosphere and only wavelength between 295-315 nm reaches Earth’s surface. Lower energy UV-A (315-400 nm) and visible light (390-750 nm) reach also the surface. Higher-energetic UV-radiation is more important in photochemistry than visible light because of reasons listed later in this chapter. However, only a few per cent (depending on many things) of radiation reaching Earths’s surface belongs to UV-band. UV-light has many disadvantages for humans and materials but it is important when creating antimicrobial, antipollution or self-cleaning properties. [39]

Titanium dioxide TiO_2 is the most studied photocatalyst and therefore it is used as an example in this chapter. Research of TiO_2 started at the beginning of the 1970’s from the Honda-Fujishima effect. A young graduate student Akira Fujishima found out that when exposing titanium oxide electrode to strong UV-light, gas bubbles were evolved from the surface of the electrode. These bubbles were oxygen and hydrogen from water that was decomposed by a photocatalytic reaction. At that time conversion efficiency was too low (0.3%) for energy conversion but despite that research continued. Later they discovered that oxidation ability of TiO_2 could be used in decomposing materials and since then many new applications have been developed including antimicrobial, self-cleaning and antipollution properties wanted from modified PEEK. [40-42]

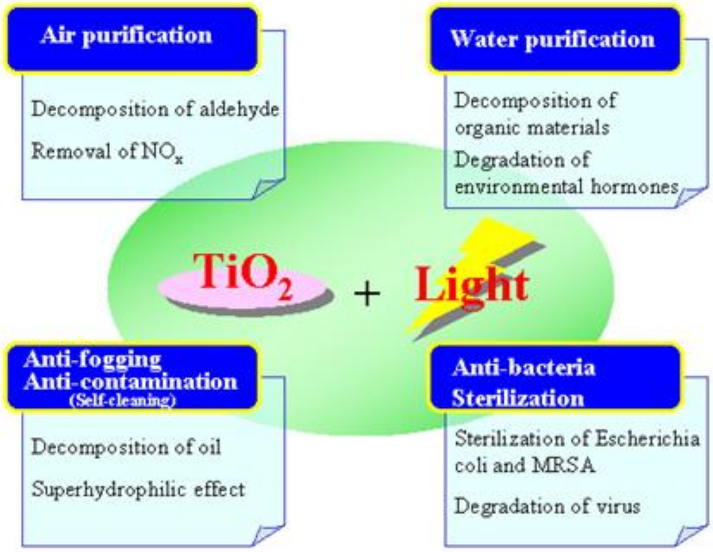


Figure 3.1. *Fundamental applications of photocatalysts. [42]*

TiO_2 is a semiconductor which means that it has band gap energy of a few electron volts. Electrons in solid materials are only within certain bands. The closer the electron is from the nucleus the smaller its energy. Valence band is the highest level where electrons are at normal state. Bands are filled from the lowest energy level first. Semiconductors have normally valence band almost full which makes it possible for the electrons to move to an upper level, conduction band. This energy difference between valence and conduction band is very important for the photocatalysis. TiO_2 have three crystal structures; anatase, rutile and brookite. Band gap of anatase, most common of these three, is about 3.2 eV. The energy of the colliding photon has to be higher than this or otherwise TiO_2 will not excite. The smaller the wavelength of the photon is the higher the energy. It is possible to calculate the wavelength from the equation

$$E=hc/\lambda \qquad (3)$$

where E is the band gap energy and h Planck’s constant 4.136 eVs. In order to excite anatase TiO_2 wavelength less than 390 nm is needed. 390 nm is in the lower boundary of visible light and therefore ultraviolet light has to be used which is one of the biggest problems of photocatalysis. This problem has been tried to solve by doping TiO_2 with various chemical compounds and make the band gap energy smaller. [41, 43, 44]

Photocatalysis reaction as an equation is simply

$$\text{Photocatalyst} \dashrightarrow e^- + h^+ \qquad (4)$$

where an electron(s) moves to a higher energy conduction band and electron-hole(s) h+ is formed in the lower energy valence band. This electron-hole is later used for oxidation purposes and the capture of the electron for reduction. However, there is a competitive reaction which is a reverse of reaction 4. Electron-hole formation and then filling it happens within the photocatalyst which drastically worsen the efficiency. This is called electron hole recombination. [41, 43]

3.2. Functional additives generally

3.2.1. Antimicrobial

Almost every class of chemical substances, including plastics, contains many kinds of microbes and their presence is almost unavoidable. However, polymers can be protected with antimicrobials (biocides), compounds that either kill the microbes or inhibit their development. These antimicrobials can be based on photocatalysis because bacteria are organic compounds which can be decomposed like any other organic material. However, many of the most commonly used antimicrobials have some other mechanism for killing microbes. Regardless the mechanism a good antimicrobial should fill a few general requirements: it should have a good affectivity in a broad spectrum, good stability, economical in use and it should be non-toxic. Micro-organisms have many subcategories like bacteria, moulds, yeast, fungi, algae and lichen. These most common growth requirements have been listed for micro-organisms in Table 3.1. [45, 46]

Table 3.1. *Growth requirements of micro-organisms. [46]*

Requirement	**Bacteria**	**Moulds and Yeast (Fungi)**	**Algae**
Light	No	No	Yes
Ideal pH	Slightly alkaline	Slightly acidic	Neutral
Ideal temperature [°C]	25-40	20-35	15-30
Nutrients	C, H, N sources	C, H, N sources	CO_2
Trace elements	Yes	Yes	Yes
Oxygen	O_2 or inorganic	O_2	O_2
Water	Liquid or vapour	Liquid or vapour	Liquid or vapour

The total consumption of antimicrobials used in 2001 was about 25 million kg which meant total revenue of 220 million dollars. Most antimicrobial additives are used for antifungal protection of flexible PVC (poly vinyl chloride) plastic. What makes PVC so vulnerable is the plasticizers that has to be used. Micro-organisms use water and plasticizers organic food sources to grow in number which degrades physical properties. Many other plastics do not need plasticizers and therefore the problem is not that severe. However, micro-organisms can cause stains and odors even when plasticizers are not used. There is a wide range of biocides available. Most commonly used biocides are OBMA (10,10’-oxybispheno arsine), OIT (n-octyl-isothiazolinone), DCOIT (4,5-di-chloro-isothiazolinone), pyrithione (mercaptopyridine-n-oxide) and BBIT (butyl-benzisothiazolinone). Triclosan (trichlorohydroxydiphenylether), metal-based biocides such as silver and photocatalytic ingredients are used mostly for getting surface effects. [46, 47]

The most widely used plastic antimicrobial additive in North America is OBMA, which gives a good protection against both fungi and bacteria. It's relatively cheap, can stand up normal processing temperatures and should be non-toxic although it has heavy metal arsine component. Because of this healthy concern, substitutes of OBMA have become more popular lately. BBIT is rather new additive that is optimized for antifungal performance. It has a good thermal stability and it does not contain heavy metals. Triclosan starts to evaporate at temperatures over 250 °C so it cannot be used with PEEK. Silver is a well-known of its biocidal properties. Its properties last long, it has a broad spectrum, good thermal stability and low volatility. However, concentration-dependent toxicity has been demonstrated with rats. In addition, European Commission and US agency for toxic substances and disease registry (ATSDR) has been concerned about heavy metal accumulation. [47, 48]

3.2.2. Self-cleaning

Self-cleaning glasses have become more and more popular during the last few years for obvious reasons. A lot of effort have been put to improve these properties and to expand the use of these materials. The basic idea of self-cleaning is a photocatalytic reaction described in chapter 3.1. Titanium dioxide, TiO_2, is the most efficient photocatalyst. In addition of its effectiveness it is also nontoxic, economical and insoluble. Self-cleaning is possible because ultraviolet light generates hydroxy radicals and superoxide ions on its surface. These radicals have very strong oxidizing and reducing power which decomposes organic waste into carbon dioxide and water. Additionally, ultraviolet light affects the TiO_2 surface by generating OH-groups which makes the surface super-hydrophilic. This makes the water pour down evenly instead of droplets and at the same time it transports the dirt with it. TiO_2 coatings are normally used in ceramics but they can be applied with polymers as well. The problem with polymers is to achieve good enough adhesion and mechanical properties [49, 50, 51]

Photocatalytic and hydrophilic reactions work together amplifying each other and enabling long lasting self-cleaning properties. Due to hydrophilicity, more OH groups are absorbed to the surface. This enhances photocatalytic reaction. On the other hand photocatalytic reaction can decompose organic compounds from the surface which improves hydrophilicity. So these two reactions are synergetic and the lack of one will drastically worsen also the other and as a result self-cleaning properties. [40]

As said before, no literature was found about properties of modified PEEK. However, TiO_2/Ag combinations have been tested to improve textiles' antibacterial and self-cleaning properties. Kiwi [52] tested cotton that was immersed in TiO_2 solution and Ag-sputtered with DC-magnetron. According to these tests it is possible to create flexible textile with strong bactericide activity with 4-5 semi-transparent layers of Ag. Self-cleaning properties were tested with wine stains and noticeable discoloration was obtained under solar light. [52]

3.2.3. Antipollution

TiO_2 and a few other chemical compounds can induce antipollution properties. Some polymers e.g. PVC has the problem that they release highly toxic dioxins into the atmosphere when burned temperatures under 800 °C. Dioxins are a major risk to humans and nature like Seveso accident in 1976 proved. Thousands of people were contaminated and tens of thousands of animals either died or had to be killed. Of course under normal circumstances the problem is not that severe but the cumulative effect can be significant at its worst. [53, 54]

Antipollution additives like TiO_2 are used to decompose toxic chemicals at the same method explained before. Generated hydroxy radicals and superoxide ions neutralize toxic chemicals. To decrease the amount of toxins, adsorption capability of TiO_2 is one of the most concerned subjects. This is because it is easier to collect toxic chemicals from a two-dimensional surface than three-dimensional space. To increase adsorption capability several experiments have been made. Surface modification with hydrofluoric acid (HF) treatment improved TiO_2/PVC composites adsorption almost 200% according to Sun’s test [53].

3.3. Benzophenone- based compounds

3.3.1. Benzophenone generally

The goal of this project is to make fiber from PEEK/benzophenone compounds. TiO_2 was used as an example in the previous chapter because there is limited amount of data available about benzophenone (BP). Benzophenone compounds are potential alternatives for TiO_2/Ag additives but they have been studied much less. They have good antimicrobial properties while being economical and environmentally safe. Microorganisms can survive days or even longer on most polymers so biocides are needed in protective clothing. BP is an aromatic ketone and important compound in organic photochemistry which for its part explains the low price. BP is also used in dyes, pesticides and even in drugs. When BP groups are in polymer matrix as photoinitiators, they can kill bacterials and even decompose organic materials under UVA (≤365 nm) light. The chemical structure of benzophenone can be seen in Figure 3.2. [55, 56]

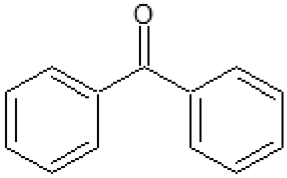


Figure 3.2. *Chemical structure of benzophenone.*

There is very little literature available of benzophenone- compounds tested with PEEK but it has been tested with several commodity plastics like polyethylene, polypropylene and polystyrene. In Hong and Sun's tests [55] 0.5 wt-% of BP was mixed with four thermoplastics: PE, PP, PS and PVA (polyvinyl alcohol) and mechanical and antimicrobial properties were tested. It was noticed that all polymers suffered some damages by the addition of BP. However, antimicrobial properties improved the more the bigger the addition of BP was. This means that compromises have to be done in order to get both good mechanical and antimicrobial properties. Some tests indicate that BP may cause unwanted yellow color because of its spectral curves [39].

There are two ways to incorporate photoiniators such as BP into the polymer. The first is the inclusion as a pendant or in a terminal position in a polymer and the second is to copolymerize it into the backbone of a polymer. Hong and Sun's test [55] belongs to the first category. Another experiment made by the same authors [56] belongs to the second group. Polystyrene was copolymerized with benzoyl chloride by Friedel-Crafts acylation and poly(styrene-co-vinylbenzophenone) was manufactured. The bigger the benzophenone content was the better photoactivity and thus antimicrobial properties were. However, when benzophenone content was too high, it became impossible to form smooth surfaces. [57]

It is important to maintain good mechanical properties when improving antimicrobial properties. Benzophenone tends to weaken fibers as Hong's [58] test indicate. Tensile strength of several benzophenone incorporated cottons decreased from 17 to as low as 9 MPa compared with pristine cotton. In the case of PEEK this kind of weakening would mean tensile strength of about 55 MPa instead of 100 MPa which could be too small for some applications. Nevertheless, antimicrobial properties were once again excellent so the biggest concern is to maintain mechanical properties. [58]

3.3.2. Benzophenone ketyl radical generation

BPK radical generation involves two phases. In the first benzophenone undergoes light-excitation to n->π* triplet states. According to IUPAC (International Union of Pure and Applied Chemistry) n->π* transition means "An electronic transition described approximately as promotion of an electron from a 'non-bonding' (lone-pair) n orbital to an 'antibonding' p orbital designated as p*" [59]. In the second phase this excited radical can abstract hydrogen atoms from reactive functional groups such as amines or alcohols. Figure 3.3 describes how BPK radical is born. [60, 61]

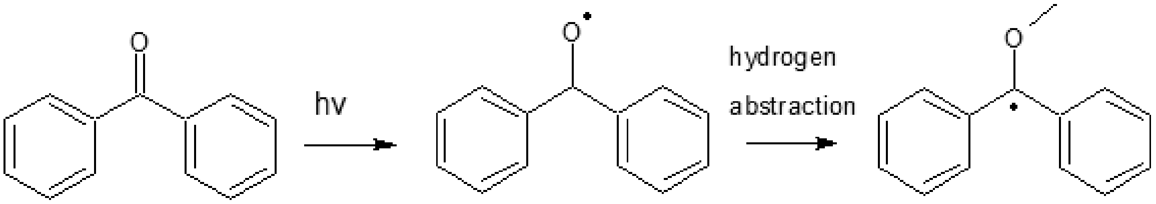


Figure 3.3. *BPK radical generation.*

After the photon has excited benzophenone, it is highly reactive toward hydrogen abstraction. Like said before, it can abstract the hydrogen from functional groups and also some polymers like PMMA (polymethyl metacrylate) and PVA can act as donors. It becomes BPK radical after it has abstracted the proton. The born radical has relatively long lifetime which, considering the applications, is a desirable property. [61]

What may become a problem is the competitive reaction of ESIPT (excited-state intramolecular proton transfer) which takes place through an IMHB (intramolecular hydrogen bond). Instead of getting the proton from an outside (intermolecular), the proton moves inside the molecule (intramolecular). This will lead to loss of photoreactivity. [62, 63]

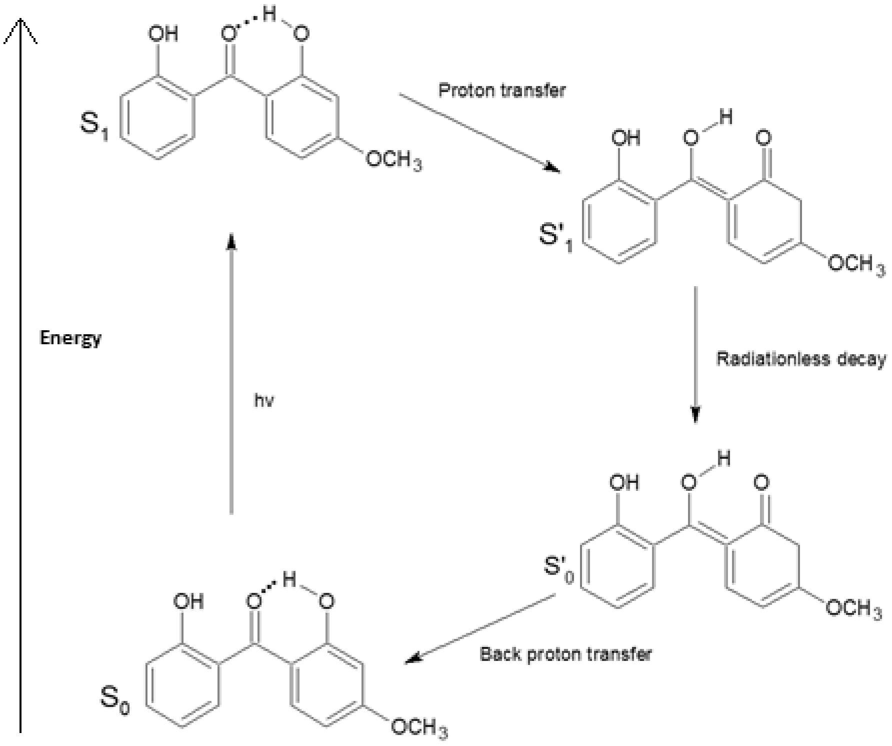


Figure 3.4. *Excited-state intramolecular proton-transfer mechanism.*

In Figure 3.4 is a schematic presentation of ESIPT. When a photon with sufficient energy hits a steady-state molecule it excites the molecule. Proton moves intramolecularly to another place in the UV-absorber and that releases some energy. More of its energy is released via radiationless decay. Back proton transfer returns the molecule to its steady-state. Overall, UV-radiation is transformed into thermal energy. This process can be very fast and happen in less than 40 ps for highly photostable molecules. [39, 62, 63]

3.3.3. PEEK modification with BPK

The problem of PEEK is that it cannot generate BPK radicals in its native state but it has to be modified with for example amino or sulphonate groups. These groups make it possible that PEEK can promote to triplet state with the help of UV-irradiation and then abstract proton from a functional group. There is a reaction formula in equation (5) for SPEEK (sulfonated polyetheretherketone) that has been irradiated with UV-light. The reaction is the same than in Figure 3.3 which means that after abstracting a proton there is the important BPK group in the polymer chain. [73-75]

$$\left[-O-\underset{SO_3^-}{C_6H_3}-O-C_6H_4-CO-C_6H_4-\right]_z \xrightarrow{hv} \left[-O-\underset{SO_3^-}{C_6H_3}-O-C_6H_4-CO^\bullet-C_6H_4-\right]_z \qquad (5)$$

There are a lot of possibilities where that proton can be abstracted. In Korchev's tests [61] SPEEK was blended with PVA which acted as proton donator. This reaction formula has been described in equation (6).

$$\begin{gathered}[-O-C_6H_4-CO^*-C_6H_4-]_z + [-CH_2-CH(OH)-]_y \rightarrow \\ [-O-C_6H_4-C^\bullet(OH)-C_6H_4-]_z + [-CH_2-C^\bullet(OH)-]_y\end{gathered} \qquad (6)$$

The born SPEEK radical has a long lifetime of about 40 minutes at room temperature. It is possible to see the effects of UV-light with naked eye because the blend changes color to pink and then decays slowly in the dark. These radicals undergo dimerization / disproportonation process which has a second-order rate constant of $k_4=700\ M^{-1}s^{-1}$ in stirred solutions. This is over 10^6 smaller than the rate constant of benzophenone in similar process in water. These two negatively charged macromolecules are the reason for this. When BPK radicals are exposed to oxygen they rapidly reoxidize to BP and form hydrogen peroxide H_2O_2. [61]

Hydrophilicity is important property in self-cleaning glasses. Like TiO_2, also SPEEK provides good hydrophilicity and thermal stability [65]. In chapter 3.2.2 was described how hydrophilicity improves self-cleaning properties and enhances photoreactivity. It is unknown whether the reaction mechanism is synergistic similarly to the case of TiO_2, but there is a good change this can be the case. More research should be done to verify this mechanism.

Geometric arrangements are important considering the possibility of ESIPT mechanism in PEEK. It is a general rule in aromatic molecules (like PEEK) that electron acceptors attract more electrons in excited state and electron-donating substituents become stronger donors. The reason for this is that ionic resonance structures contribute significantly more to the excited states than to the ground state. In order to the ESIPT to be efficient the molecule has to be in planar structure and the process is also influenced by polarity of the molecule. If the polymer is modified by twisting the aromatic rings ESIPT will become impossible and the polymers' photoactivity increases. [39] This is one possible reason that PEEK has to be modified with example sulfonate groups in order to inhibit the intramolecular proton transfer. However, literature does not give straight answers for the mechanism.

Formation of intermolecular H-bonds in matrices with H-acceptor moieties can lead to interruption of IMHB. This will improve photoreactivity because it makes ESIPT impossible. This H-tunneling is possible in polymers that have construction units with basic moieties capable of intermolecular H-binding with acid phenolic hydoxy groups presented in Figure 3.5. [39] Theoretically also this can be the reason that sulfonated groups dampen the ESIPT mechanism. More research should be carried out to verify the mechanism.

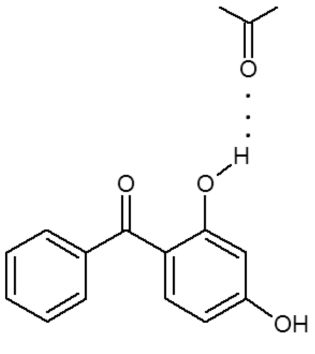


Figure 3.5. *Intermolecular hydrogen bonding of 2-hydroxybenzophenone.*

The degree of sulfonation of PEEK affects the mechanical properties of the polymer. Post sulfonation of PEEK degrades the mechanical and thermal stabilities and also makes the control of the process much more difficult. More advanced method is the direct synthesis of SPEEK from sulfonated monomers. This helps to prevent unwanted cross-linking and other side reactions and also allows better control of the degree of sulfonation.

Li’s and co-workers’ tests [69] show that mechanical properties were best when sulfonation ratio (m/k, where k is 4,4-difluorobenzophenone monomer and m is sodium 5,5-carbonylbis(fluorobenzene-sulfonate) monomer) was as small as possible or exactly 1:1. Small changes in the sulfonation ratio made a significant difference to mechanical properties which has to be taken into consideration when manufacturing the polymer. [66]

4. Characterization

Before fiber spinning tests can be started, PEEK has to be characterized thermally and rheologically. Thermal tests give information about the possible processing temperatures and times. The material should not degrade during the time it spends in the barrel. Rheological tests are important because they provide information how viscosity changes as a function of temperature. This information is useful when choosing the optimal grade and later during the spinning tests.

4.1. Rheology

Rheological measurements were carried out with Göttfert Rheograph 6000 capillary rheometer, which will later be used for making the filament yarns. Test samples of PEEK were obtained from Victrex and the grades were 381G and 151G. The purpose of these measurements was to observe how PEEK behaves rheologically and also test the Göttfert capillary rheometer at high temperatures (360 °C and 380 °C). Moisture absorption of PEEK is so small that pellets were not dried before the tests. Generally preliminary tests went better than expected. Only one drawback happened during 381G 360 °C measurements when pressure built up too high and the sensor had to be changed from 140 to 200 MPa and then repeat the test. Göttfert's barrel is 12 mm in diameter and capillary 30 mm long, 1 mm in diameter (L/D=30) and has one hole.

Test was repeated at three different temperatures to characterize the rheological properties of PEEK. Test parameters were the same as in the first test and a pressure sensor of 140 MPa was used. Viscosities vs. shear rate curves can be found in Figure 4.1.

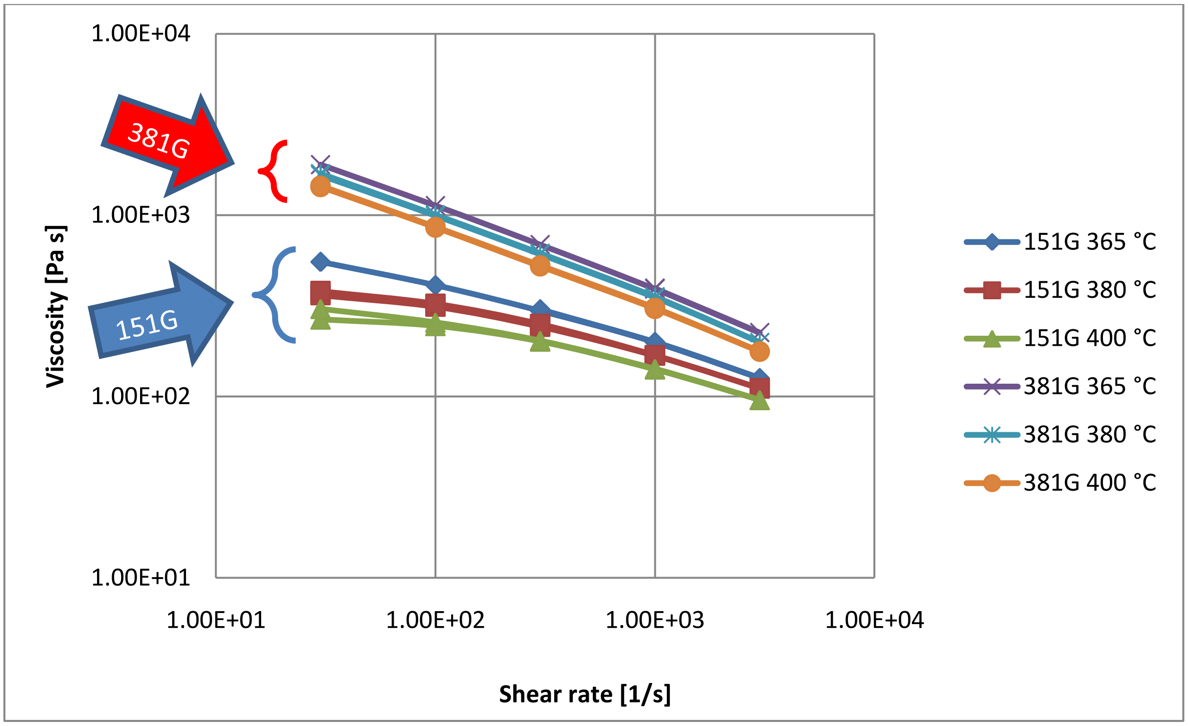


Figure 4.1. *Viscosity tests for grades 151G and 381G. Measurements were carried out from low shear rates to high and then back.*

Behavior of PEEK was predictable. At logarithmic scale the viscosity curves are almost straight lines. Measurement were carried out from low shear rates to high and then back. Points were almost exactly the same place regardless the direction which means that no thermal degradation or other problems happened during the measurements. Grade 381G (number follows from melt viscosity according to Victrex own test TM-VX-12 which is carried out at 400 °C and shear rate 1000 1/s [25]) has higher viscosity than 151G.

The second test clearly shows that grade affects much more to the viscosity than temperature. 151G in 365 °C flows much better than 381G in 400 °C. Shear thinning was bigger when using grade 381G and especially at low shear rates the difference was noticeable. More tests should be carried out at low shear rates to test rheological properties at similar conditions to actual fiber spinning. Tests were carried out from low shear rates to high and then back and only one point was slightly different at the second measurement. During the experiment it was tested to manually create thin PEEK fibers by drawing them very quickly by hand. This technique allowed creating fibers less than 100 µm in diameter and general impression was that PEEK fibers should be easy to manufacture.

Our Italian partner company NTT, Next Technology Technotessile, provided a small amount of Victrex PEEK grades 450G and 704 to test their rheological properties. Assumption that the number means melt viscosity was right for the 450G but wrong for the 704. Tests were carried out with the same parameters than the previous tests (capillary 30 mm / 1 mm) except that 200 MPa pressure sensor was used. Test curves can be found in Figure 4.2.

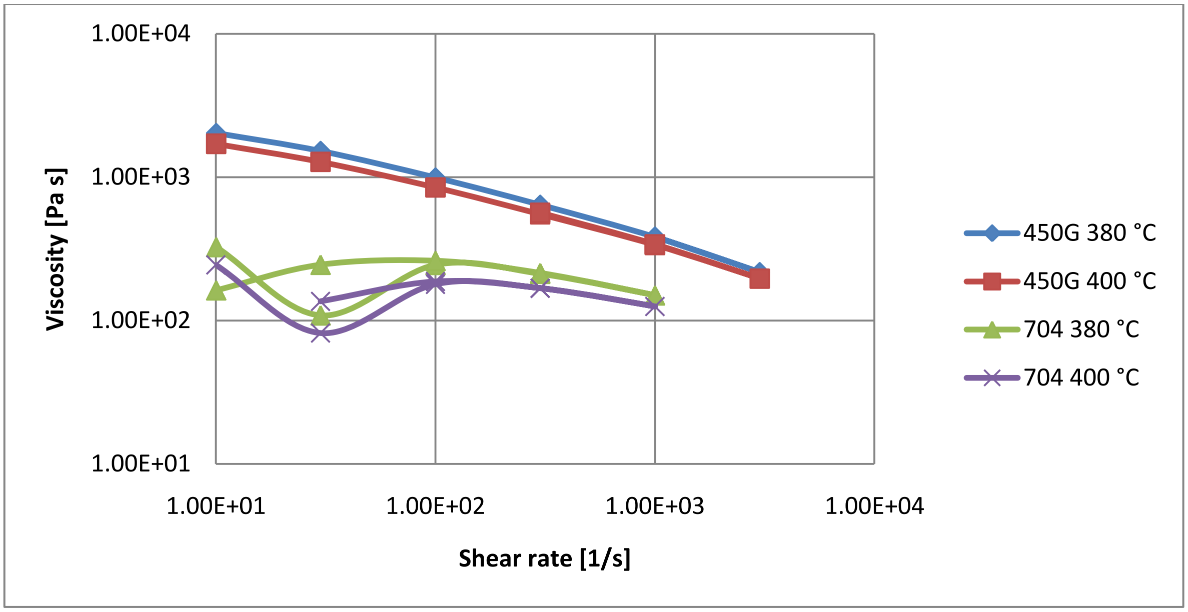


Figure 4.2. *Viscosity tests for grades 450G and 704. Measurements were carried out from low shear rates to high and then back.*

The viscosity curve of the grade 450G is almost similar to 381G which is not surprising considering that they are both depth filtered grades with nearly the same viscosity number. Everything went as planned and no problems arose during the tests. Unfortunately this was not the case with 704 which is a powder grade. Material was hard to load into the barrel because it glued to the barrel walls. During the 380 °C test the machine made bad noises and vibrations which can be the first signs of a machine failure. It was decided that grade 704 will no longer be used in temperatures lower than 400 °C.

Melt viscosity of grade 704 was even smaller than 151G. Because of insufficient information, 200 MPa pressure sensor was used and it turned out to be too high. This can partly explain the inconsistent results at low shear rates.

4.2. DSC tests

DSC (Differential Scanning Calorimetry) tests were performed to see whether PEEK suffers from thermal degradation. Tests were carried out in Netzsch DSC 204 F1 heat-flux DSC. In heat-flux DSC test sample and reference are heated in the same chamber with one heater. This differs from the power-compensating DSC which has separate heaters for the sample and the reference. Because of different thermal properties and certain chemical reactions, the sample and the reference warm up at a different rate. Heat flows through a metal disk to the sample and the reference and differential thermocouples measure the differential temperature signal. This is normally measured in electric voltage difference. If the same amount of heat flows to the sample and to the reference the potential difference is then zero. When some kind of transition (like melting) happens in the sample, differential signal is generated. Difference in heat flow rates is proportional to this difference in electric voltage. A typical heat-flux DSC system is presented in Figure 4.3. [67, 68]

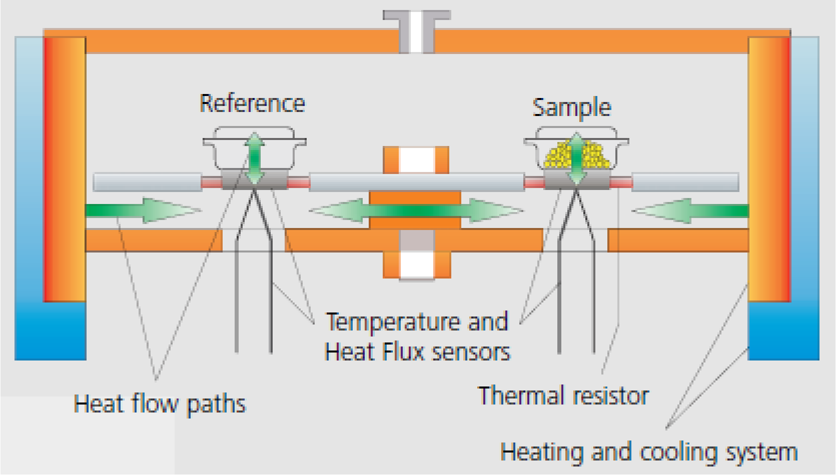
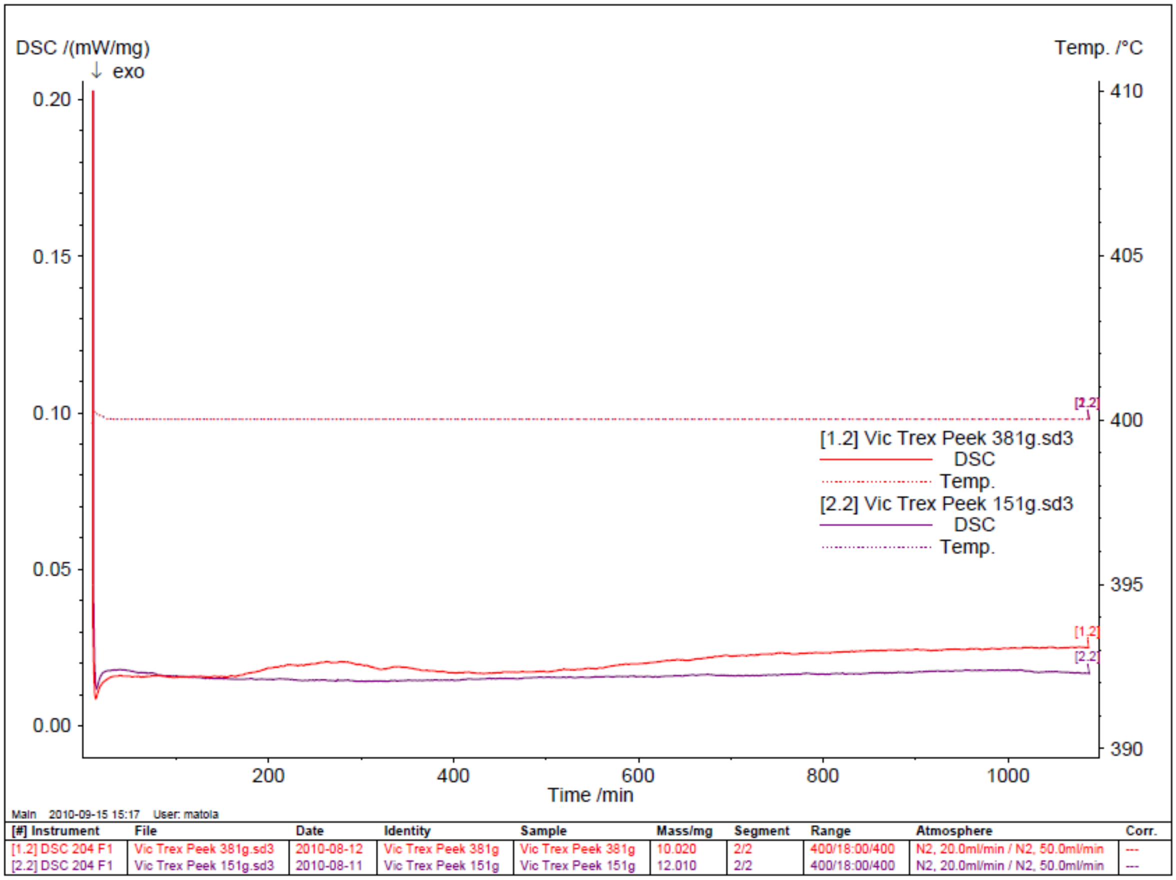


Figure 4.3. *A heat-flux DSC. [71]*

Victrex PEEK grades 151G and 381G were heated to 400 °C and kept at that temperature overnight. 400 °C was chosen because it is the upper processing temperature and during the melt spinning one test drive can last several hours. If PEEK starts to degrade in the barrel it has immediate effects on viscosity and mechanical properties. Tests were performed in nitrogen-atmosphere because capillary rheometer is nearly a closed space and therefore PEEK is not in contact with oxygen. The results of these tests can be seen in Figure 4.4.



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[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1.2] DSC 204 F1	Vic Trex Peek 381g.sd3	2010-08-12	Vic Trex Peek 381g	Vic Trex Peek 381g	10.020	2/2	400/18:00/400	N2, 20.0ml/min / N2, 50.0ml/min	---
[2.2] DSC 204 F1	Vic Trex Peek 151g.sd3	2010-08-11	Vic Trex Peek 151g	Vic Trex Peek 151g	12.010	2/2	400/18:00/400	N2, 20.0ml/min / N2, 50.0ml/min	---

Figure 4.4. *Overnight DSC curves of PEEK at 400 °C.*

It is easy to notice that both grades are relatively stable. There were small variations in nitrogen flow with grade 381G and therefore its test was repeated. Retest showed that 381G is thermally as stable as 151G.

More DSC-tests were carried out to see whether anything unusual emerges. But traditional DSC-tests revealed nothing new (see Appendix 2). PEEK was first heated from a room temperature to 400 °C at a rate of 20 °C/min, then cooled down to room temperature and then heated again to 400 °C to see if any thermal history exists. Curves clearly show the good stability PEEK has. Curves of heated and re-heated PEEK are almost similar so there is no evident thermal history. Glass transition is barely visible or the unevenness may also be something else. The two grades have slightly different rheological properties and molar mass distributions and therefore grade 151G melts in narrower range and it has higher peak than 381G. Onset temperature for melting is around 325 °C and the peak is near 340 °C for both grades.

4.3. TGA tests

TGA (Thermogravimetric analysis) tests show how plastics lose mass as a function of temperature or time. Chemical reactions may take place during the heating but they do not affect the mass unless components evaporate. Tests were carried out to see how PEEK degrades thermally and especially how it behaves near the processing temperatures. [69]

PEEK was heated in a nitrogen atmosphere at a rate of 10 °C/min from a room temperature to 1000 °C. Tests were carried out twice for both grades. Test curves were similar enough so there was no need to add both curves. These TGA-tests can be found in Appendix 3. Literature says that auto-ignition temperature is about 570 °C and TGA tests support this. The weight loss is relatively insignificant up to temperatures of about 550 °C after which the weight loss derivate increases rapidly achieving the maximum at about 590 °C. Test results did not reveal anything new or surprising. The only significant difference between the two grades is that 151G lost 60% of its mass whereas 381G over 66%. For melt spinning this is not however relevant because processing temperatures are much lower.

5. Experimental Part

5.1 Melt spinning equipment

A typical melt spinning machine has been described in chapter 2.3. The basis of our system is Göttfert Reograph 6000 capillary rheometer. It has a maximum working temperature up to 400 °C and a volume of about 26 cm^3. Barrel is 12 mm in diameter and 230 mm in length. The material is loaded into the barrel and a piston presses it through a capillary hole. TUT melt spinning machine can be seen in Figure 5.1. Piston is removable and it is not attached to the machine in the figure.

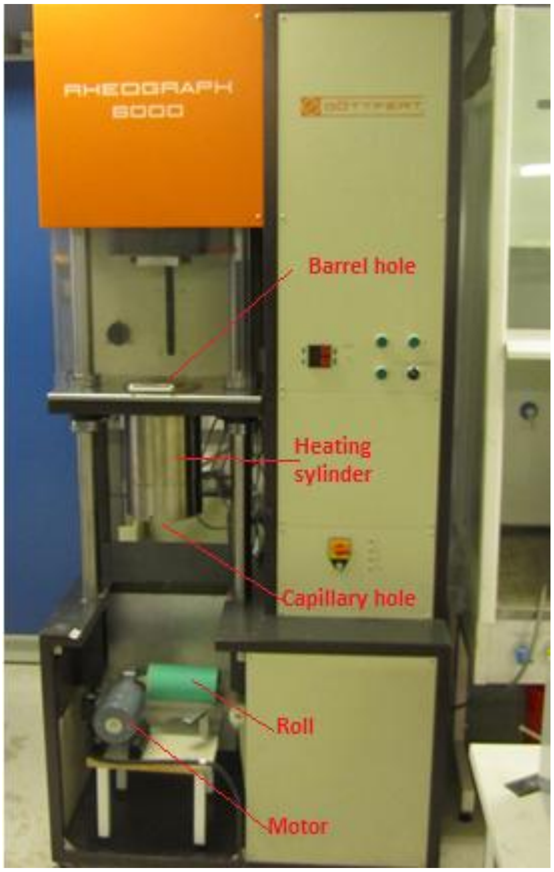

Figure 5.1. *Melt spinning system in TUT.*

Below the capillary there is a motor that winds the PEEK to a roll. The motor system in use is borrowed from the Institute of Fibre Materials Science and it consists of three separate motors and a control unit. Motor speed can be varied manully from zero to 3000 RPM. However, the motor has a gear that reduces the maximum speed to about 350 RPM.

This value was measured with a tachometer. At very low RPM the motor runs unevenly but this happens only below 20 RPM.

There are a few requirements for a good motor for melt spinning. It should have a variable speed and easy control for acceleration. Many electric motors have problems in low speeds because they start to vibrate which can lead to filament breakages. Motor should run extremely smoothly at high speeds. Maximum speed is not very relevant because fibre diameter or speed can be varied by changing the diameter of the take-up roll or the speed of the piston. A screen for the precise RPM would be a nice bonus because it would make it possible to evaluate the born filaments theoretically. Unfortunately the motor we borrowed does not include this property. Despite that flaw the preliminary tests showed that the motor is capable of winding thin PEEK fibers.

Without the borrowed motor the plan would have been to buy an AC servo motor. AC servo motors are commonly used in industrial applications that require accurate control. These motors fulfil all the requirements for melt spinning but they are rather expensive. This is because a separate control unit has to be bought. Winding of thin filaments does not require much power or torque from the motor. However, for example Mitsubishi recommends that load inertia should be smaller than 15 times the inertia of the motor. A 50 W motor can weight as little as 350 g. [70] This power would be enough but the physical size of the motor could mean problems with high-mass take-up rolls. Increasing the size and the inertia of the motor will most likely decrease vibrations at high speed. ,

5.2 Optimal spinning parameters

5.2.1 The first tests and material selection

Finding the optimal parameters requires time and a lot of trials and failures. Therefore the chosen grade should be not only easy to spin but also easy to load into the barrel and clean afterwards. So far Victrex grades 151G, 381G, 450G and 704 have been tested. The first three are granulates and the last is a powder. It was decided to choose the right grade between these four. The most valued properties have been listed in Table 5.1. Price of these grades is fairly similar.

Table 5.1. *Material selection table.*

Grade	**151G**	**381G**	**450G**	**704**
Fiber properties	Good	Moderate	Moderate	Very good
Loading	Easy	Easy	Easy	Difficult
Cleaning	Normal	Difficult	Difficult	Normal

Fiber properties are very much dependent on the viscosity. Grade 704 has the lowest viscosity and during the first tests thinnest fibers were made from it. Grade 151G has a little higher viscosity than 704. The fiber formation of grade 151G is almost as good as grade 704. Grades 381G and 450G have higher viscosity and also fiber formation is worse.

When using PEEK, capillary rheometer is hard to clean and it can take up to two hours to clean it after the use. This lost time during the cleaning could have been used to test the parameters. None of the grades is easy to clean. However, low viscosity grades 151G and 704 seem to be easier to clean than 381G and 450G for some reason. Especially the walls of piston are hard to clean after PEEK has stick to them at high pressure. This problem is more severe with grades 381G and 450G.

The third criterion is easy loading to the barrel. 151G, 381G and 450G are granulates and they are easy to load. Grade 704 is a powder which leads to problems described in chapter 4.1. Without that flaw, grade 704 would have been the best candidate but this problem rules it out. This makes the grade 151G to be the best candidate for finding the limits of the process. 5 kg of this grade was ordered from Mape Plastics which is the Nordic reseller of Victrex PEEK.

It has to be remembered that properties vary even within the grade. For Victrex 151G the melt viscosity tolerances are between 120-180 Pa s. Test shipment had the viscosity of 170 Pa s and the bigger shipment of 140 Pa s (measured by Victrex). Viscosity tests were remade at 400 °C to see whether they differ from the test shipment. The results of these tests can be found in Table 5.2.

Table 5.2. *Viscosity differences between shipments at 400 °C.*

Shear rate [1/s]	30	100	300	1000	3000
Viscosity of test shipment [Pa s]	285	250	202	142	96
Viscosity of bigger shipment [Pa s]	209	196	164	119	82

It's easy to notice that although the grade is the same, the properties can vary very much between the shipments. Especially at low shear rate (30 1/s) new shipment flows much better. The difference could be even greater at very low shear rates during the fiber spinning. This should be mostly a good thing because lower viscosity improved fiber quality according to the preliminary tests.

Theoretical calculations are important because they provide an easy way to evaluate spun fibers. In theoretical calculations piston speed v_{piston} is considered to be accurate. The godet roll diameter and motor speed have been measured and they should be fairly accurate. When calculating fiber diameter it is easier to start with DDR (draw down ratio) which is defined as the ratio of fiber speed near the winder and near the capillary. Unit of d_{godet} is [m], d_{piston} and $d_{capillary}$ [mm] and v_{piston} [m/s]. d_{godet} is normally 87 mm, and d_{piston} 12 mm.

$$DDR = \frac{v\mathrm{l}}{v\mathrm{o}} = \frac{\boldsymbol{\pi d}\mathrm{godet}\left(\frac{\mathbf{350}\ \boldsymbol{RPM}}{\mathbf{60}}\right)}{\left(\frac{\boldsymbol{d}\mathrm{piston}}{\boldsymbol{d}\mathrm{capillary}}\right)^2 \boldsymbol{v}\mathrm{piston}} \quad (7)$$

Because mass flow has to be constant for continuous processes, fiber diameter Ø can be calculated from DDR and capillary diameter. DDR has no unit and both $d_{capillary}$ and Ø are in [mm].

$$\emptyset = \frac{\boldsymbol{d}\mathrm{capillary}}{\sqrt{\boldsymbol{DDR}}} \quad (8)$$

Tex-number is commonly used to measure size in many products like cables and fibers. One tex tells how much 1000 m of something weights. Decitex is even more common than tex and it tells the mass of 10 000 m long fiber. It can be calculated if the fiber diameter and density of the material are known. Unit of dtex is [g/10 000m], Ø [mm] and ρ [g/cm^3].

$$dtex = \frac{\boldsymbol{\emptyset^2 \pi \rho}}{\mathbf{4 * 10^{-4}}} \quad (9)$$

Fiber diameter can be calculated also from the mass throughput if the take-up speed v_l of the fiber is known. The machine is kept at a constant velocity for a few minutes and the time and the mass of the fiber are measured. The unit of mass m is [g], take-up speed v_l [cm/s], time t [s], density [g/cm^3]. This equation gives the fiber diameter in [cm].

$$\emptyset = 2\sqrt{\frac{\boldsymbol{m}}{\boldsymbol{\pi t \rho v} l}} \quad (10)$$

Theoretical mass throughput can be calculated from the piston speed. The unit of mass throughput is [g/min], v_{piston} [cm/s] and density ρ [g/cm^3]. The density of PEEK is about 1.32 g/cm^3 at solid state. The density above the melting point is unknown and probably varies a function of temperature so therefore value 1.32 g/cm^3 has been used. This may cause some inaccuracy. r_{piston} is 0.6 cm.

$$\boldsymbol{m}\mathrm{throughput} = \boldsymbol{v}\mathrm{piston} * (\boldsymbol{r}\mathrm{piston})^2 * \pi * \rho * 60 \frac{s}{min} \quad (11)$$

5.2.2 Processing temperature

The idea of spinning tests is to find optimal parameters and the limits of spinnability in this system. Because the motor has no RPM screen it will be used at full speed (350 RPM). This is much easier and more accurate than using the same mass throughput. Fiber diameter is changed by decreasing the mass throughput (piston speed) in stages. Motor will be accelerated slowly to the maximum speed and kept there for 60 seconds. If the filament breaks the test will be repeated at least five times at that mass throughput. If the process is stable after those 60 seconds then piston speed (mass throughput) will be decreased until the limit is found.

Capillary rheometer is not designed for fibre spinning. This became apparent during the early tests when small amounts of PEEK dripped out of the capillary at high temperatures. So at very low piston speeds PEEK flows out itself. Pressure sensor was used to evaluate this because if the pressure is zero then piston speed is slower than the spontaneous flow. Test was carried out with 1 mm capillary at 400 °C. With smaller capillaries and lower temperatures the problem is not as severe because viscosity gets higher. This test shows that with these parameters the limit is about 2 1/s shear rate which means piston speed of about 0.0017 mm/s. This means that it is impossible to create fibers thinner than 12 µm in diameter according to equations 7 and 8 in our equipment at these parameters.

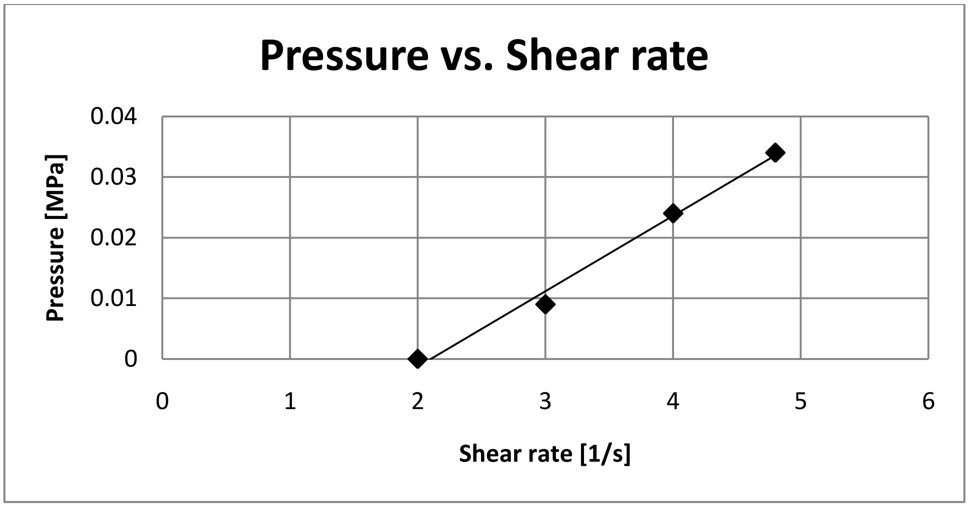

Figure 5.2. *The limit of spontaneous flow.*

Feasibility study showed that higher temperature should improve spinnability and decrease filament breakages. Three different temperatures, 370 °C, 385 °C and 400 °C, were selected for testing. Capillary was 1 mm in diameter. Tests were done during several days. The first day was used to find a rough estimate of the limit and the latter days were used to improve and verify the results of the first day. The final results can be seen from Table 5.3.

Table 5.3. *Fibre diameter in three different temperatures.*

Temperature	370 °C	385 °C	400 °C
Shear rate [1/s]	7.9	4.8	4.6
Lowest stable piston speed [mm/s]	0.0069	0.0042	0.0040
Theoretical mass throughput [g/min] (11)	0.062	0.038	0.036
Theoretical diameter [µm] (8)	25	19	19
Theoretical draw down ratio (7)	1600	2700	2800
Theoretical tex-number [dtex] (9)	6.5	3.7	3.7
Measured mass throughput [g/min]	0.047	0.036	0.029
Calculated diameter from the mass throughput [µm] (10)	32	18	17
Diameter measured with thickness meter [µm]	27	23	18
Pressure during measurement [MPa]	0.26	0.12	0.06

As one can see differences were significant between temperatures. At 370 °C it was difficult to get the process stable even at higher piston speeds because fiber diameter varied all the time. This was easily visible to naked eye. At 385 °C these fluctuations were not as visible and process was more stable. As a result, also diameter of the spun fibers was smaller. Temperature's raise from 385 to 400 °C improved spinnability only a little. Before tests low piston speeds were estimated to be a problem for starting the process. Fortunately at higher temperatures Victrex PEEK 151G flowed very well out of the capillary and the spinning initiation took only seconds instead of estimated several minutes.

Measurements with thickness meter and the mass-time measurement are only rough estimates for the fiber diameter. The problem with thickness meter is that it flattens the fiber and therefore the values are too low. The average thickness of 20 different fibers was measured. Deviation is huge with thickness meter. The problem with mass measurements is that some PEEK has always come out of the capillary before the time starts. Therefore a long measuring time (10 min) was used to improve reliability. These two tests were done to see whether theoretical values are reliable because of the spontaneous flow. The results seem to be fairly consistent. In chapter 5.4.2 can be found the results of the optical microscope and they confirm that theoretical calculations as well as these measurements should be fairly accurate. Tests show that the thinnest achieved fiber should be less than 20 µm in diameter.

5.2.3 Capillary dimensions

During the early tests it became apparent that very large (>1 mm) capillaries cannot be used because material flows out spontaneously. 1.5 mm capillary was tested and with it the process was stable even without piston movement.

Also shorter capillaries were pretested and ruled out. The process was not stable. This was unfortunate because it would have been interesting to see how capillary length affects spinning properties. Longer capillaries orientate the fiber better which should theoretically mean better fiber quality. The reason for this unstable process is most likely the hot air PEEK faces when it comes out of the capillary. Infrared radiation coming from all directions makes the fiber more vulnerable for breaking. If a full length capillary (30 mm) is used then the air is much cooler. During the tests with shorter capillaries (16 and 20 mm) it was very difficult to start the winding and in the best case the process was stable for only a few seconds. The fundamental reason for this problem is that capillary rheometer is not designed for fiber spinning. Figure 5.3 clarifies the problem of short capillaries.

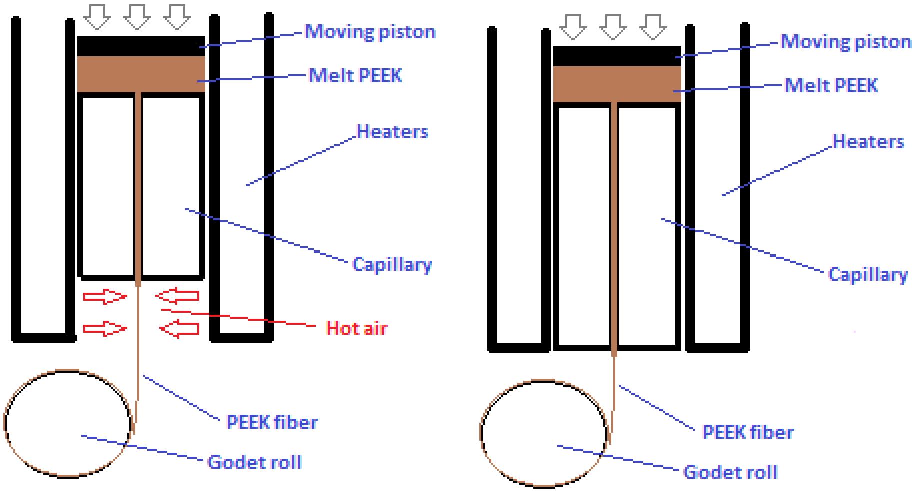

Figure 5.3. *A short capillary and a long capillary.*

Finally, only two capillaries were suitable for testing: 30 mm / 1 mm and 30 mm / 0.75 mm. This is unfortunate because capillary dimensions are very important parameters. Larger capillaries could not be used because PEEK flows out them spontaneously and smaller capillaries were too expensive to manufacture. Tests were carried out at 400 °C and full motor speed.

Table 5.4. *Fiber diameter with two different capillaries.*

Capillary diameter [mm]	1.0	0.75
L/D-ratio	30	40
Best stable piston speed [mm/s]	0.0040	0.0066
Shear rate [1/s]	4.6	18.0
Stable pressure [MPa]	0.06	0.35
Theoretical mass throughput [g/min] (11)	0.036	0.059
Theoretical fiber diameter [µm] (8)	19	24
Theoretical draw down ratio (7)	2800	940

Theoretical tex-number [dtex] (9)	3.7	6.0
Measured mass throughput [g/min]	0.029	0.048
Calculated diameter from the mass throughput [µm] (10)	17	22
Diameter measured with thickness meter [µm]	18	24

Theoretically bigger capillary diameter should provide improved spinning stability [34]. This is very apparent also in our tests. Theoretical fiber diameter worsened from 19 to 24 µm when decreasing the diameter. It would have been interesting to see the results with 0.5 mm capillary but unfortunately this was not possible.

5.2.4 Other parameters

Length of the spinning path is an important parameter in commercial applications. The spinning path can be several meters long at most. The room under the capillary rheometer is less than a meter and therefore very extensive tests are not needed or possible. All the tests so far have been done with 40 cm spinning path.

First it was tested what is the shortest possible spinning path at 400 °C, 1 mm capillary and full motor speed. The fiber has to solidify so that it will not stick to other fibers or to the roll. Because there is only one thin monofilament it cools rapidly. Therefore no problems were detected even at very short cooling paths (<5 cm).

The limit of spinnability was tested at 5 cm spinning path, 400 °C temperature, 1 mm capillary and full motor speed and the results were compared with previous tests. The results are in Table 5.5.

Table 5.5. *The effect of the spinning paths length.*

Length of the spinning path [cm]	40	5
Best stable piston speed [mm/s]	0.0040	0.0035
Shear rate [1/s]	4.6	4.0
Theoretical mass throughput [g/min] (11)	0.035	0.031
Theoretical fiber diameter [µm] (8)	19	18
Theoretical draw down ratio (7)	2800	3200
Theoretical tex-number [dtex] (9)	3.7	3.3

The results are slightly better with shorter spinning path and the best so far. The thinnest achieved theoretical fiber diameter improved from 19 to 18 µm. In addition to this the process was much more stable at higher piston speeds than before. The reason for this is most likely decreased turbulence. At 40 cm spinning path air movements vibrate the fiber noticeably which can affect the process stability. At 5 cm spinning path no vibrations were visible. Thickness meter was not used and mass throughput was not measured because they are not accurate enough to see differences this small.

5.3. PEEK modification and mixing

5.3.1. PEEK modification (NTT)

Sulfonated PEEK was modified by Next Technology Technotessile, NTT, which is our research partner company from Italy. NTT has been working hard to modify and test different kinds of modified PEEK grades but they have not managed to publish anything yet. Therefore no data is available from the modification process. More about used methods and materials is available in the near future after the first publications.

5.3.2. Mixing of modified PEEK

NTT provided us a small amount of sulfonated PEEK. This sulfonated PEEK was mixed with Victrex grade 151G which is the grade spinning limits were tested. Mixing was done with DSM Xploren TM micro compounder. It has two screws rotating to the same directions, a maximum volume of 5 cm^3 and maximum temperature of 400 °C. Because of the tiny volume and difficult cleaning, sample preparation turned out to be very slow.

First mixing trials were made at 3 % concentration. Mixer was loaded almost full, then the screws rotated 10 min at 200 RPM and then the material was unloaded. Processing temperature was 360 °C. This was repeated a few times so that about 15 g of material was manufactured. Material changed its color during the mixing and it seemed to be fairly homogenous. This was the case also in the DSC-analysis in chapter 5.3.4, because there are no visible phase changes in the curve. All the following mixtures were manufactured at the same processing parameters. 15 g of material is not enough to fill the whole barrel and therefore the amount was increased to 30 g. Preparation of material needed to fill the barrel once takes about 8 hours.

5.3.3. Fibre spinning of modified PEEK

Fiber spinning experiments started with 3 % concentration. It was challenging to get the the modified material into the barrel because of its shape and size. Unmodified PEEK was tested to be ductile but even 3 % addition of sulfonated PEEK makes it very brittle.

Test parameters were selected according to previous tests with unmodified PEEK. This turned out to be a mistake because modification clearly changes PEEK’s chemical structure, viscosity and thermal properties. At 380 °C and 1 mm capillary modified PEEK comes out of the capillary like a fluid. During the first trials fiber spinning was not successful.

Tests continued with 1 % sulfonated PEEK concentration and different processing parameters. Processing temperature was decreased to 345-365 °C and capillary to 0.75 mm to decrease spontaneous flow. With 1 % SPEEK addition it was possible to manufacture fibers. Suitable processing temperature was 360 °C. The quality of these fibers was mediocre at best. The process was stable about 20 s at piston speed 0.018 mm/s (shear rate 50 1/s) which means fiber thickness of 40 μm. The color of these modified fibers is brownish whereas the natural PEEK fibers are blond.

After successful trials concentration was increased to 2 %. Increase in sulfonate-concentration clearly makes the spinning more difficult. At 2 % the process was stable only for a few seconds at best. Changing the sulfonate-concentration also changes the processing parameters. This and the lack of material make the fiber spinning even more difficult.

The last tests were done with 1.5 % concentration and 355 °C processing temperature. Previous tests have shown that the higher SPEEK concentration is the lower should the processing temperatures be. The process was stable about 20 s at best at a piston speed of 0.0183 mm/s (shear rate 50 1/s). The results are similar to 1 % concentration. However, the spinning technique with sulfonated PEEK is somewhat tricky and the skills improved during the tests which could have affected the results. The 1.5 % spun filaments have the thickess of about 40 μm and decent quality without any visible variations in fiber thickness.

5.3.4 Characterization of sulfonated and modified PEEK

The testing of sulfonated PEEK and modified PEEK was limited because of the lack of time and materials. Rheological tests could not be done because sufficient amounts of material could not be manufactured. Sulfonation clearly changes mechanical properties and it makes the fibers more brittle. Unfortunately there was not enough time for full scale mechanical testing.

TGA tests and DSC tests were done for both sulfonated PEEK and 1 % modified PEEK. The results are in Appendix 2 and 3. Sulfonated PEEK decomposes thermally so that at 550 °C it has lost over half of its weight. As a comparison, unmodified PEEK loses less than a per cent of its weight at 550 °C. For this reason DSC tests for sulphonated PEEK had to done to at 220 °C instead of 400 °C. It is obvious that something has changed between the first and the second heating because the curves are at totally different places. According to the TGA tests something has evaporated from the sample. 1 % modified PEEK is thermally almost as stable as unmodified PEEK starting to lose mass from above 550 °C

Although the tests could not be done during this Master of Science thesis, the project will continue and then full scale testing will be done. In chapter 5.4 is described the tests that were done to unmodified PEEK grade. These same tests will be done later to modified PEEK, preferably at different modification concentrations. The results of photochemical tests are very interesting because these reactions are needed to provide functional properties. These tests will be done by NTT during the next few months.

5.4 Characterization of melt-spun fibers

5.4.1. Mechanical properties

In order to test the mechanical properties of the unmodified PEEK fibers a test sample of 25 µm fiber was prepared at 400 °C with 1 mm capillary. This is not the absolute minimum for fiber diameter but it was chosen because very thin fibers tend to break easily and therefore sample preparation is much harder. Test was done according to a standard ISO 5079:1995 "Textiles fibres - Determination of breaking force and elongation of individual fibres" with Lenzing Vibroskop and Vibrodyn. Instead of recommended 50 measurements only 20 was done because PEEK is a synthetic fiber and it causes problems with Vibroskop. There was a problem to get the fiber to vibrate. First Vibroskop was used to determinate the tex-number and then the same fiber was stretched until breaking. The advantage of measuring the tex-number first is the more accurate data because fibre cross-sectional density is known. More precise data about the test parameters can be found in the test diary in Appendix 4.

From the test data it is very easy to draw a few conclusions. The first is that the fiber diameter is not homogenous. Tex-number varies within 3.1 and 9.9 decitex average being 6.2. Tensile strength's average is 2.2 cN/dtex which means about 280 MPa (ratio is 100ρ). The standard deviation of tensile strength is very small, only 0.24 cN/dtex. Elongation at break varies a lot more. The average is 150 % which is much more than anticipated. It's easy to notice that thick fibers have higher elongation at break. This could mean that there is a limit in thickness near 10 µm where PEEK fibers break. Fiber parts that have stretched relatively more during the winding cannot stretch a lot during the tensile testing and vice versa. Young's modulus at 1 % elongation is higher with thinner fibers average being about 19.7 cN/dtex (2.6 GPa). More data is available at Appendix 4.

The Victrex grade 151G which was tested had very small viscosity probably as a result of a small molecular weight. This means that many of the mechanical properties are inferior compared to many higher viscosity grades [71]. Mechanical properties improve during orientation and therefore many of the properties should be better than non-orientated PEEK has [33, p. 48-65]. A small comparison between tested PEEK fibers and literature values for non-orientated PEEK can be seen in Table 5.6.

Table 5.6. *Comparison table of PEEK properties.*

	Tensile strength	Young's modulus	Elongation at break
Tested 151G PEEK fiber	260 MPa	2.6 GPa	150 %
Literature value (not orientated)	100 MPa	3.6 GPa	50 %

Tensile strength and elongation at break are almost three times as high as literature values but Young’s modulus is a little smaller. Tested values could have been higher if the chosen grade would have been higher viscosity (molar mass) grade [71].

It is possible to calculate fiber diameter from the measured tex-number with equation (9). Average tex-number 6.2 dtex equals average fiber diameter of 24 µm. This is very close to that 25 µm which is supposed to be the average.

5.4.2. Optical microscope

Fiber diameter was also measured with an optical microscope with 1000x magnification. Bunch of fibers was spread into a glass. Microscope had a rotating measuring scale which was used to read the diameter. Total of 60 fiber diameters was measured average being 25 µm and standard deviation 5.2 µm. Minimim value was 14 µm and maximum 36 µm. It was very clear that the diameter is not homogenous but varies a lot. A photo of PEEK fiber taken with optical microscope can be seen in Figure 5.4.

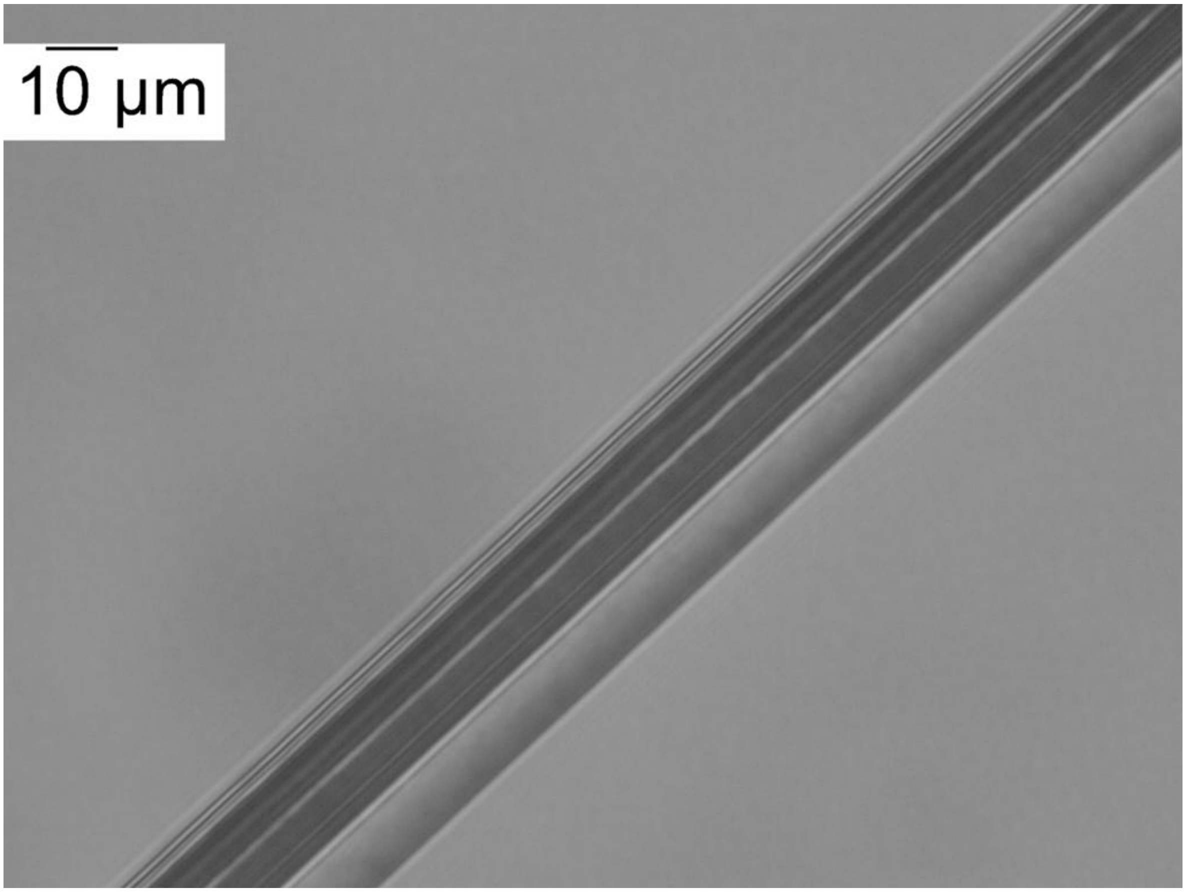

Figure 5.4. *PEEK fiber in optical microscope.*

5.4.3. Scanning electron microscope

SEM (scanning electron microscope) was used primarily to take photos of PEEK fibers. In Figure 5.5 is a bunch of PEEK fibers. From that photo it is very easy to see the huge variations in fiber diameter. The reason for these variations is clearly visible later in the next chapter in thermal imaging picture 5.8. There are some unknown particles with fibers, probably just dust. A close-up photo of PEEK fiber's surface can be seen in Figure 5.6. Surface quality is good and only very small particles are visible on the surface.

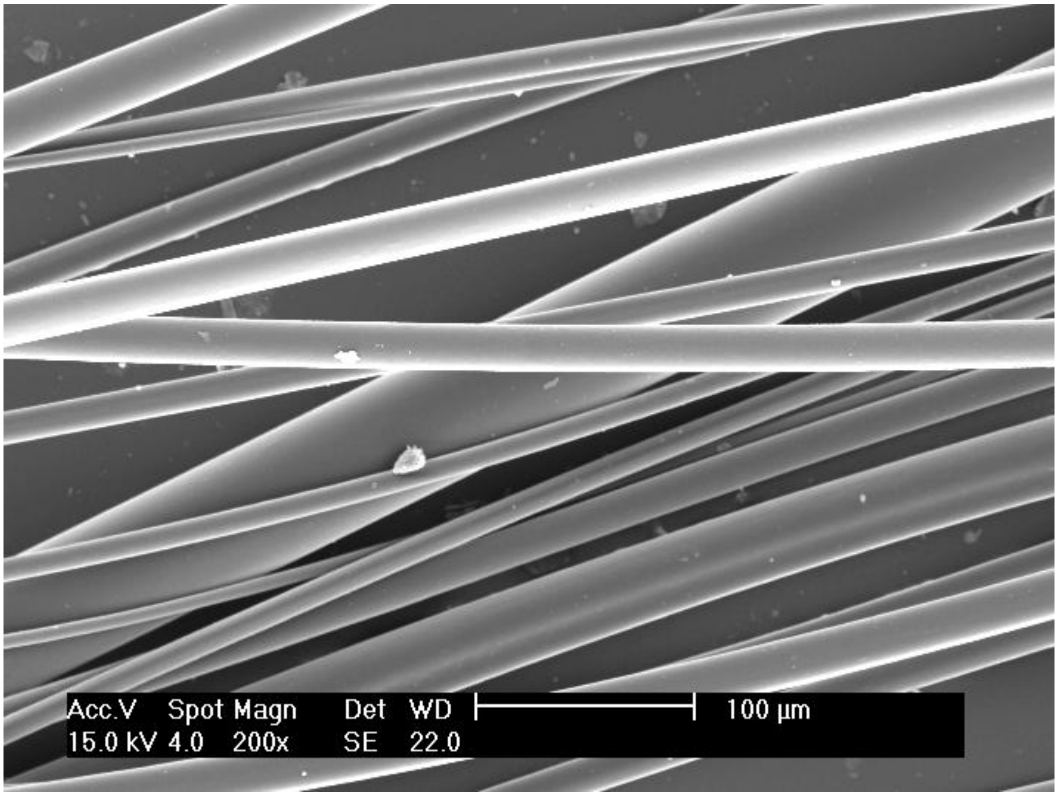

Figure 5.5. *Bunch of PEEK fibers.*

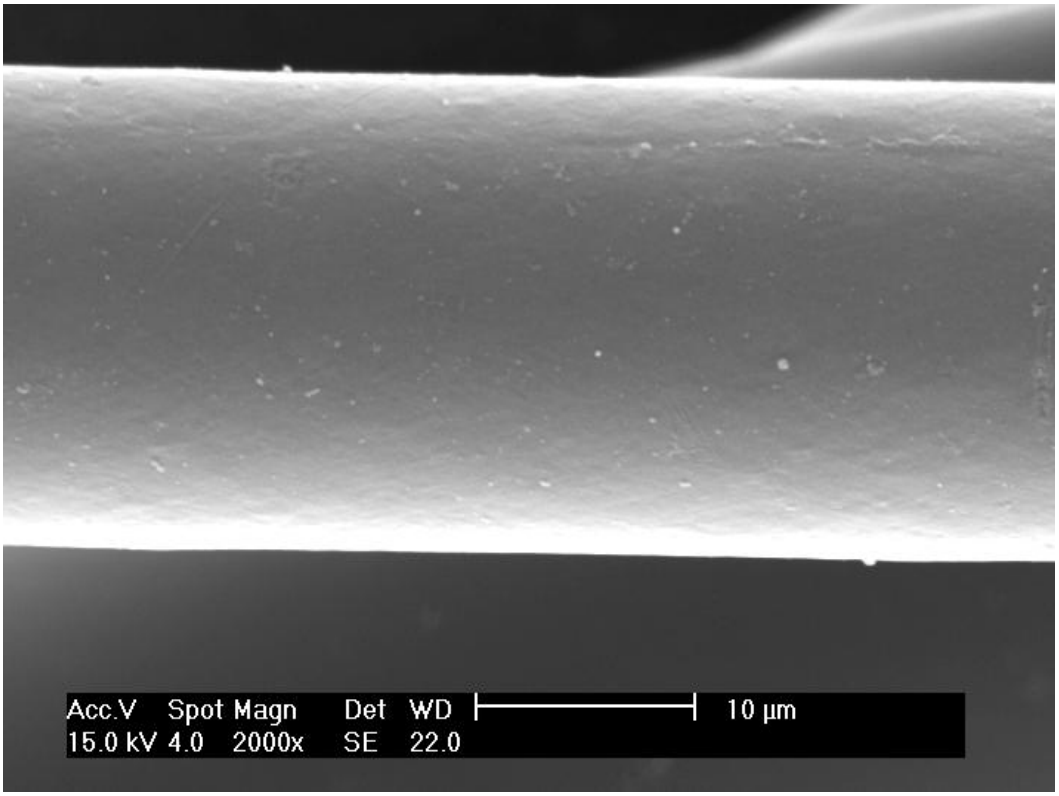

Figure 5.6. *A PEEK fiber.*

5.4.4. Thermal imaging camera

Thermal imaging camera Flir ThermaCAM PM 595 was used to observe fibers thermal behaviour. There were no high expectations beforehand because fiber is very thin (<50um) and the camera’s resolution is low. Winded filaments were purposely thicker than normally so that something would be visible in the picture. The structure of the capillary rheometer is not optimal for thermal imaging. The first centimeter of the fibers path is inside the pipe and out of the reach of the camera. A lot of thinning happens during that first centimeter. Test temperature was 380 °C and winder was 10 cm below the capillary hole. Thermal camera was placed at a distance of 50 cm from the fiber. PEEK has a thermal emissivity coefficient of 0.95.

As estimated, there were difficulties to see the fiber in the picture because it is so thin (Figure 5.7.). In most pictures the fiber was not visible. However, thermal imaging camera is very useful to see the fluctuations in fiber thickness. Previous tests have shown that material throughput and fiber diameter are not steady. Thick fiber parts cool down more slowly and this is possible to see in thermal picture. Figure 5.8 shows a cluster of thick fiber parts. It was possible to see that these kinds of clusters were formed about once in a second which means that there came roughly 3-5 thicker part in a second. Despite the big fluctuations the fiber did not break during the tests.

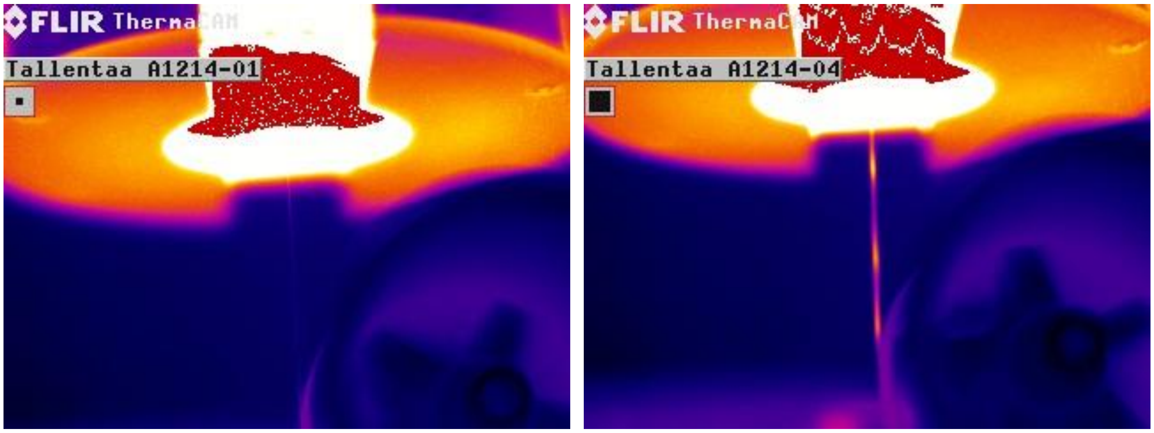

Figure 5.7. and 5.8. *Thermal imaging pictures.*

6. Conclusion

The goal of this project was to manufacture fibers of PEEK and modify the material so that the fibers could provide antimicrobial, self-cleaning and antipollution properties. These goals were mostly accomplished as fibers of unmodified PEEK could be manufactured and also modification process was successful. Unfortunately SPEEK has problems with thermal properties and fiber quality. Time to test the modified fibers was limited and therefore the results are partly incomplete. Fortunately the project will continue after this Master of Science thesis and modified PEEK can be tested thoroughly.

Theoretically PEEK has excellent thermal properties and our tests confirm this. PEEK starts to degrade at 550 °C according to TGA tests. DSC tests in constant 400 °C temperature show that PEEK can withstand high temperatures for long periods. During the melt spinning process PEEK may be hours in high temperatures so good thermal stability is needed. Rheological tests confirm that the PEEK’s grade affects more to the viscosity than temperature at the four tested grades. From the several tested PEEK’s grades, Victrex PEEK 151G was selected for large-scale testing. The decision was based not only on fiber properties but also on how easy the material is to load and clean. In addition to excellent thermal properties, PEEK should also have good mechanical properties and chemical resistance. The grade selected for testing has a low molar mass and viscosity and therefore mechanical properties are not as good as they could be. However, low viscosity grades provide good spinnability compared with higher viscosity grades.

There are several parameters in melt spinning process that have effect on fiber quality. Our equipment, Göttfert capillary rheometer, rules out some possibilities because it is not designed for fiber spinning. Experimental test results are mostly similar to the results of the literature review. Processing temperature was the most important parameter in our tests in addition to the grade. Fiber quality improved dramatically when rising the temperature, especially at low temperatures. Only a few different capillary dimensions could be tested because of practical problems. The best capillary turned out to be 1 mm in diameter and 30 mm long. There is not much space under the Göttfert’s capillary and therefore very long spinning paths could not be tested. Fortunately very thin fibers cool down rapidly and long spinning paths are not needed. The process turned out to be more stable at very short spinning paths because of decreased turbulence. Motor speed was not used as a parameter because TUT motor system has no revolution counter. During the tests the motor was used at full speed.

A representative sample of PEEK fiber was manufactured and mechanical tests were done. Optimal microscope, SEM and thermal imaging camera were used to characterize the fibers. It was noted that variations in fiber thickness are significant. Mechanical properties are a small disappointment but this is most likely because of the selected low-viscosity grade. Taken thermal imaging pictures clearly show the fluctuations in mass throughput and therefore in fiber thickness.

PEEK sulfonation was successful and it provided functional properties according to NTT. The development of sulfonated PEEK and other modified grades is in progress and therefore NTT has not provided any literature of the modification process. They sent 30 g of sulfonated PEEK which was tested and mixed with virgin PEEK. The sulfonated PEEK has to be mixed with virgin PEEK because it has poor thermal properties and inferior fiber quality. Whereas PEEK can be warmed up to 500 °C without any significant weight loss, SPEEK starts to degrade almost immediately when heated. The biggest concern of this project is that whether there is any SPEEK left at the normal processing temperatures. The photochemical tests will be carried out later by NTT. The best spinnable concentration so far was 1.5 % of SPEEK.

The best unmodified fibers were about 18 μm in diameter. To get even thinner fibers improvements should be done to the equipment. The biggest flaws are that mass throughput (fiber diameter) varies too much and there happens no mixing inside the barrel which affects material’s homogeneity. Piston movements should be fairly accurate but after the capillary material builds up and therefore fiber diameter fluctuates. This problem is probably more universal than the second problem which is a direct consequence of Göttfert’s structural flaws. Also the motor should be better to get very thin fibers. The motor system that was used during the tests works properly but with very thin fibers there is zero tolerance for vibrations or rough accelerations. The modified material should be developed to improve thermal properties. This is probably the hardest part of the project. New materials are currently being tested by NTT hoping they bring improvement to this problem.

There is a lot of testing left that has to be done after this Master thesis. In the latter part of the project testing of the modified PEEK will continue and the process will be scaled up. The mechanical, optical microscope and SEM tests for modified fibers will be done. It is too early to say whether real-world applications are possible. A lot depends on how well those modified low-concentration PEEK fibers provide functional properties. If they do, protective PEEK suits for complex emergency operations are one step closer to come true.

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[75] Korchev, A.S., Bozak, M.J., Slaten, B.L., Mills, G., Polymer-Initiated Photogeneration of Silver Nanoparticles in SPEEK/PVA Films: Direct Metal Photopatterning. *J. Am. Chem. Soc. 126(*2004)10.

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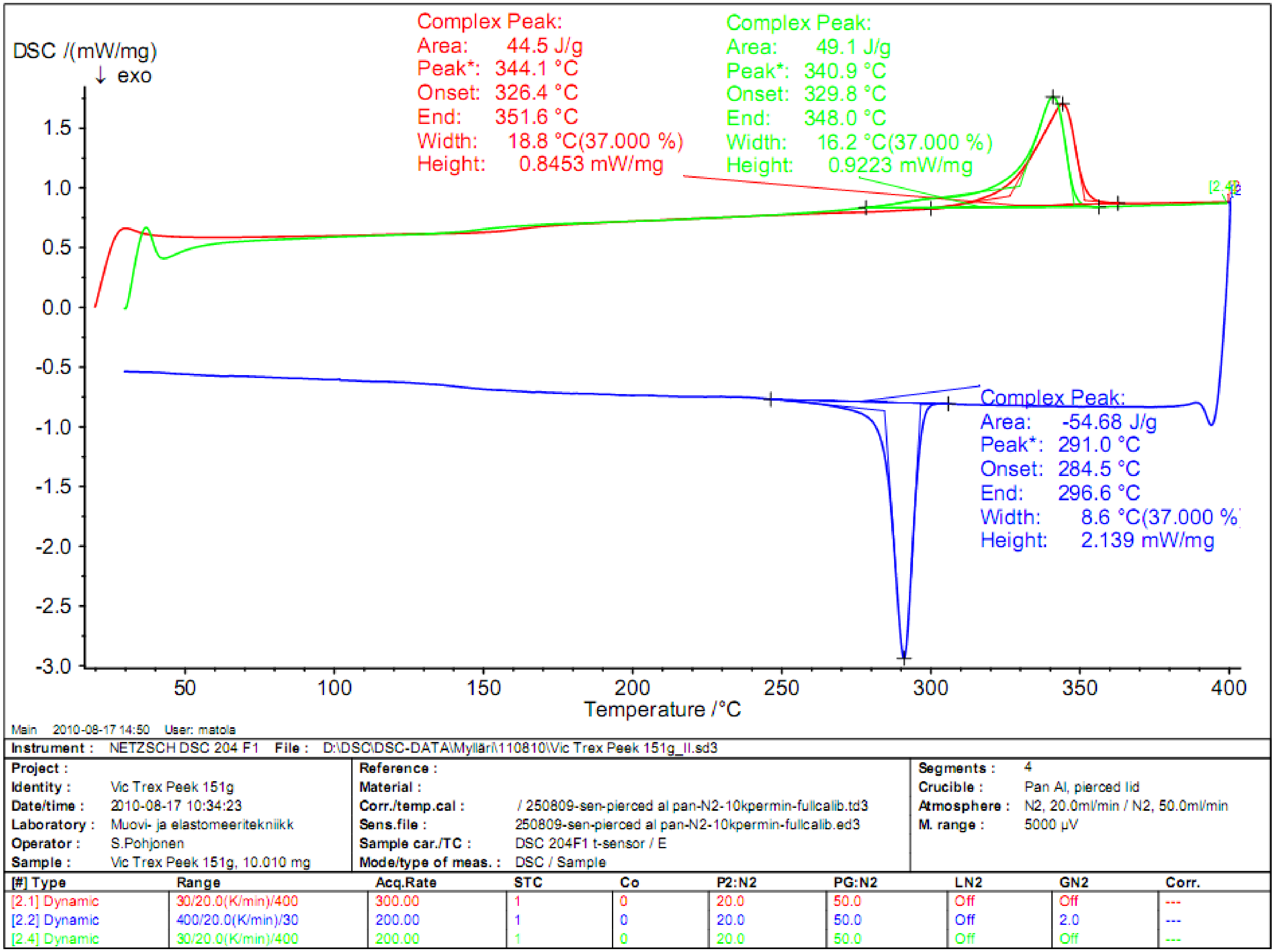
APPENDIX 1: PROPERTIES OF PEEK

Density [g/cm^3]	1.32
Tensile yield strength [MPa]	89.6
Tensile strength [MPa]	97-100
Flexural strength [MPa]	170
Compressive strength [MPa]	118
Young's modulus [GPa]	3.6
Flexural modulus [GPa]	4.1
Hardness [Rockwell]	126
Elongation at break [%]	50
Dynamic friction ratio	0.25
Impact strength, Izod notched [J/m]	85.4
Poisson's ratio	0.39
Glass transition temperature [°C]	146
Max. working temperature [°C]	260
Melting point [°C]	343
Processing temperature [°C]	360-400
Autoignition temperature [°C]	570
Thermal conductivity [W/(m K)]	0.2
Thermal expansion [10^{-6}/°C]	47
Heat capacity [kJ/(kg °C)]	2.16
Water absorption, saturated [wt-%]	0.5
Mould shrinkage [%]	1
Electric conductivity [% IACS]	$3.45*10^{21}$
Electric resistivity [Ωm]	$5.0*10^{23}$
Price, in 2010 [EUR/kg]	100
Sources: [1-4, 33]	

APPENDIX 2: DSC-CURVES OF PEEK



Main 2010-08-17 14:50 User: matola

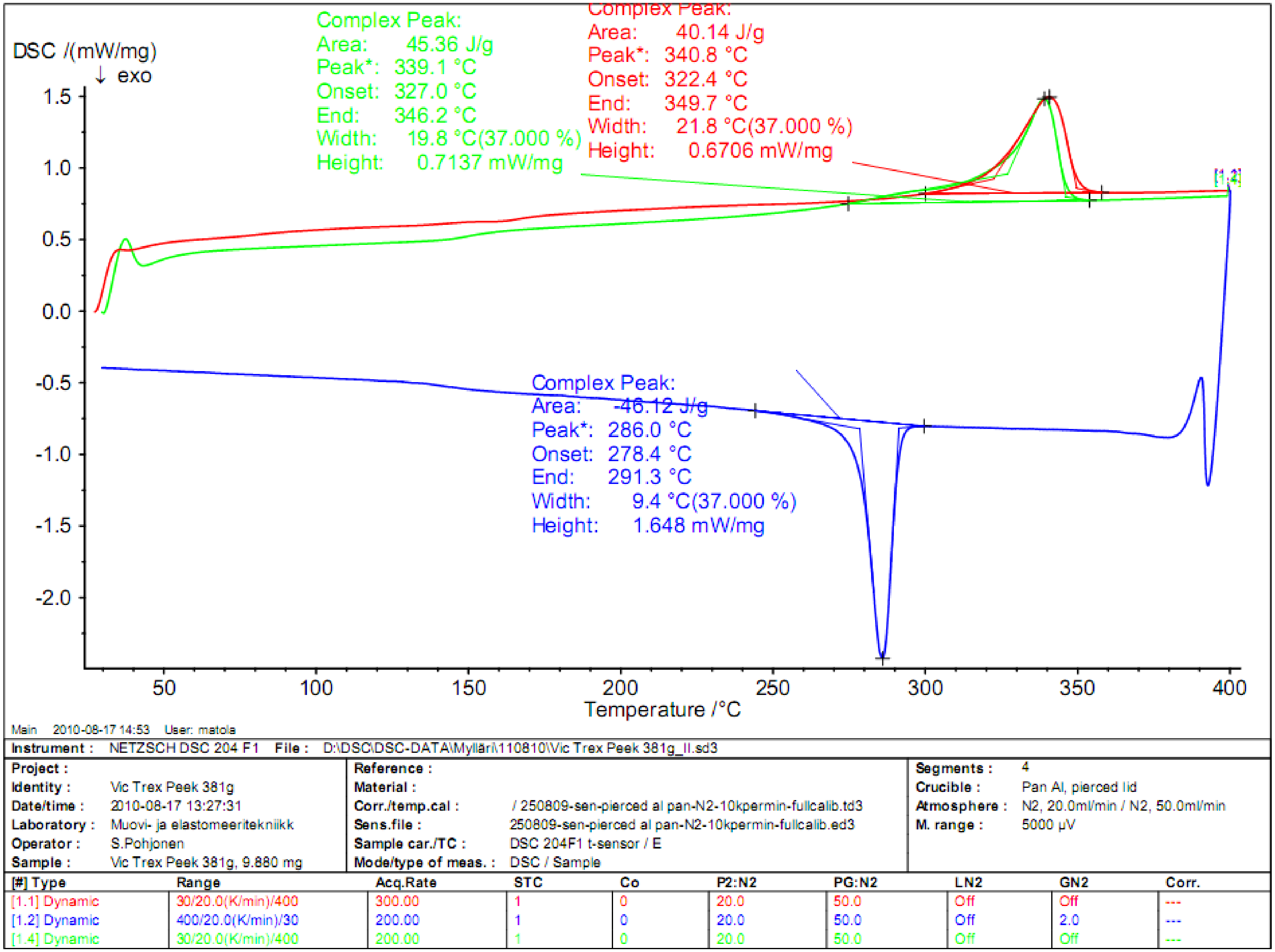
Instrument : NETZSCH DSC 204 F1 **File :** D:\DSC\DSC-DATA\Myllări\110810\Vic Trex Peek 151g_II.sd3

Project :
Identity : Vic Trex Peek 151g
Date/time : 2010-08-17 10:34:23
Laboratory : Muovi- ja elastomeeritekniikk
Operator : S.Pohjonen
Sample : Vic Trex Peek 151g, 10.010 mg

Reference :
Material :
Corr./temp.cal : / 250809-sen-pierced al pan-N2-10kpermin-fullcalib.td3
Sens.file : 250809-sen-pierced al pan-N2-10kpermin-fullcalib.ed3
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / Sample

Segments : 4
Crucible : Pan Al, pierced lid
Atmosphere : N2, 20.0ml/min / N2, 50.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	Co	P2:N2	PG:N2	LN2	GN2	Corr.
[2.1] Dynamic	30/20.0(K/min)/400	300.00	1	0	20.0	50.0	Off	Off	---
[2.2] Dynamic	400/20.0(K/min)/30	200.00	1	0	20.0	50.0	Off	2.0	---
[2.4] Dynamic	30/20.0(K/min)/400	200.00	1	0	20.0	50.0	Off	Off	---



Main 2010-08-17 14:53 User: matola

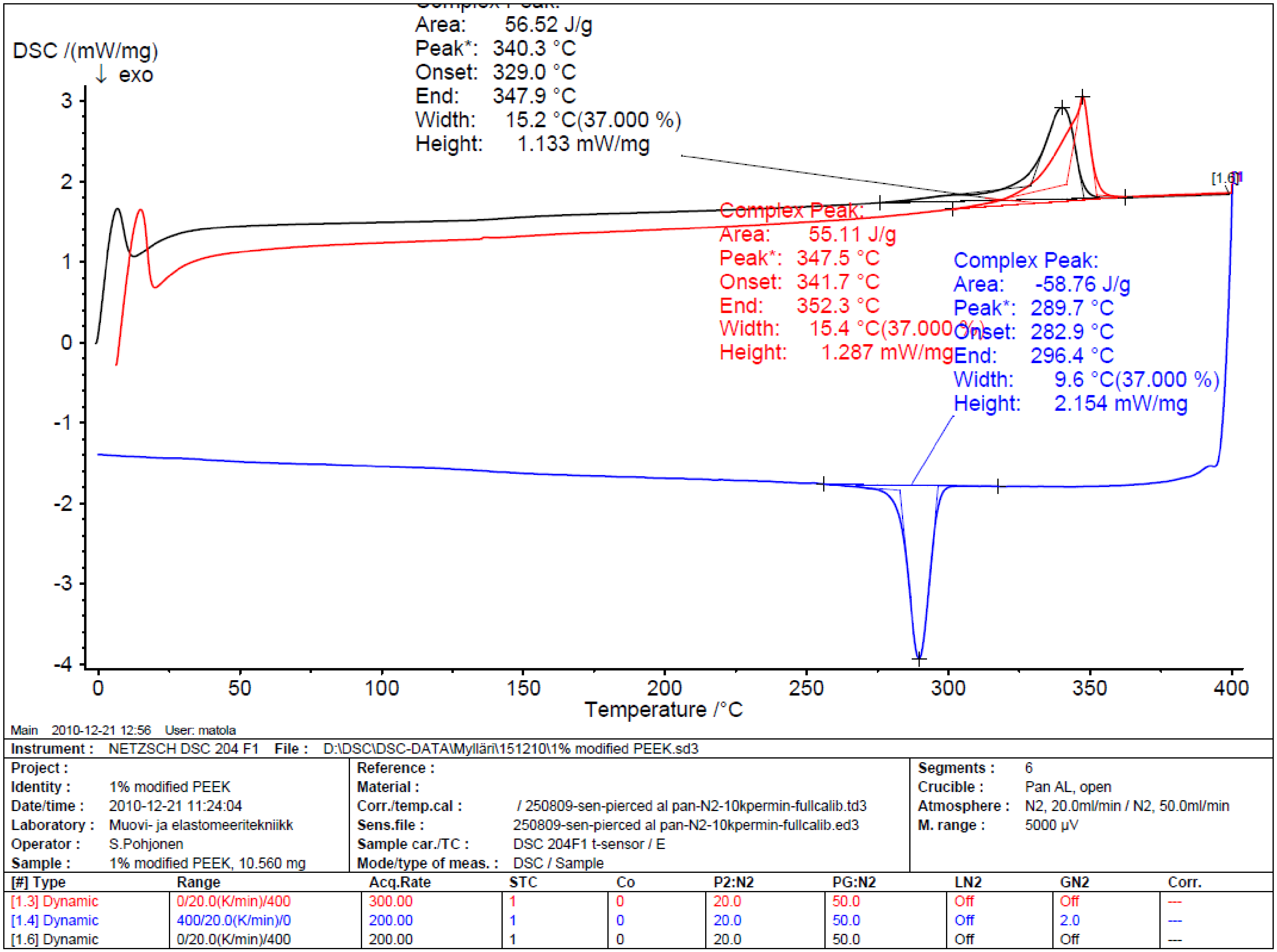
Instrument : NETZSCH DSC 204 F1 **File :** D:\DSC\DSC-DATA\Mylläri\110810\Vic Trex Peek 381g_II.sd3

Project :
Identity : Vic Trex Peek 381g
Date/time : 2010-08-17 13:27:31
Laboratory : Muovi- ja elastomeeriteknIikk
Operator : S.Pohjonen
Sample : Vic Trex Peek 381g, 9.880 mg

Reference :
Material :
Corr./temp.cal : / 250809-sen-pierced al pan-N2-10kpermin-fullcalib.td3
Sens.file : 250809-sen-pierced al pan-N2-10kpermin-fullcalib.ed3
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / Sample

Segments : 4
Crucible : Pan Al, pierced lid
Atmosphere : N2, 20.0ml/min / N2, 50.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	Co	P2:N2	PG:N2	LN2	GN2	Corr.
[1.1] Dynamic	30/20.0(K/min)/400	300.00	1	0	20.0	50.0	Off	Off	---
[1.2] Dynamic	400/20.0(K/min)/30	200.00	1	0	20.0	50.0	Off	2.0	---
[1.4] Dynamic	30/20.0(K/min)/400	200.00	1	0	20.0	50.0	Off	Off	---



Main 2010-12-21 12:56 User: matola

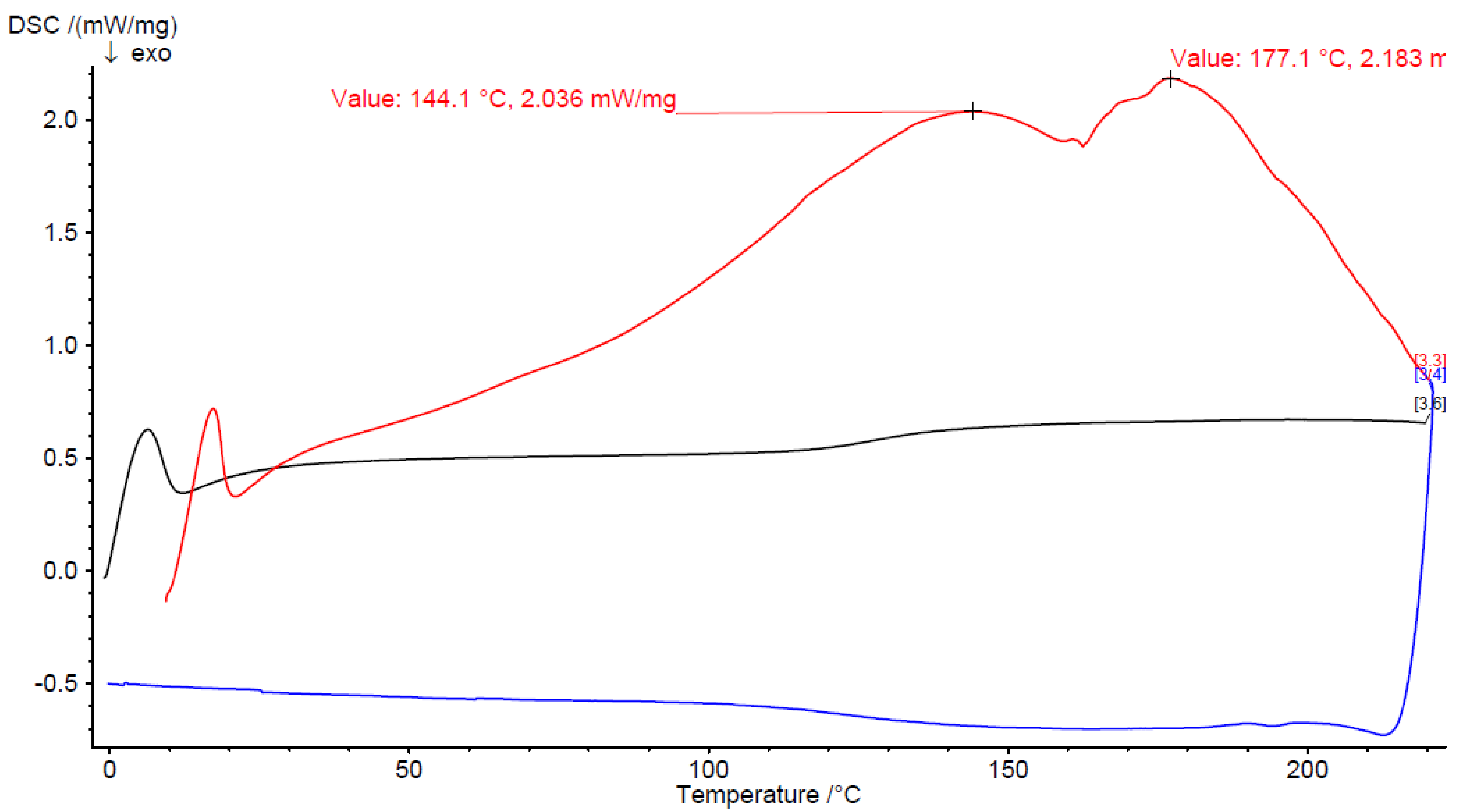
Instrument : NETZSCH DSC 204 F1 **File :** D:\DSC\DSC-DATA\Mylläri\151210\1% modified PEEK.sd3

Project :
Identity : 1% modified PEEK
Date/time : 2010-12-21 11:24:04
Laboratory : Muovi- ja elastomeeritekniikk
Operator : S.Pohjonen
Sample : 1% modified PEEK, 10.560 mg

Reference :
Material :
Corr./temp.cal : / 250809-sen-pierced al pan-N2-10kpermin-fullcalib.td3
Sens.file : 250809-sen-pierced al pan-N2-10kpermin-fullcalib.ed3
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / Sample

Segments : 6
Crucible : Pan AL, open
Atmosphere : N2, 20.0ml/min / N2, 50.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	Co	P2:N2	PG:N2	LN2	GN2	Corr.
[1.3] Dynamic	0/20.0(K/min)/400	300.00	1	0	20.0	50.0	Off	Off	---
[1.4] Dynamic	400/20.0(K/min)/0	200.00	1	0	20.0	50.0	Off	2.0	---
[1.6] Dynamic	0/20.0(K/min)/400	200.00	1	0	20.0	50.0	Off	Off	---



Main 2011-01-12 10:30 User: matola

Instrument : NETZSCH DSC 204 F1 **File :** D:\DSC\DSC-DATA\Mylläri\100111\sulfonated_II.sd3

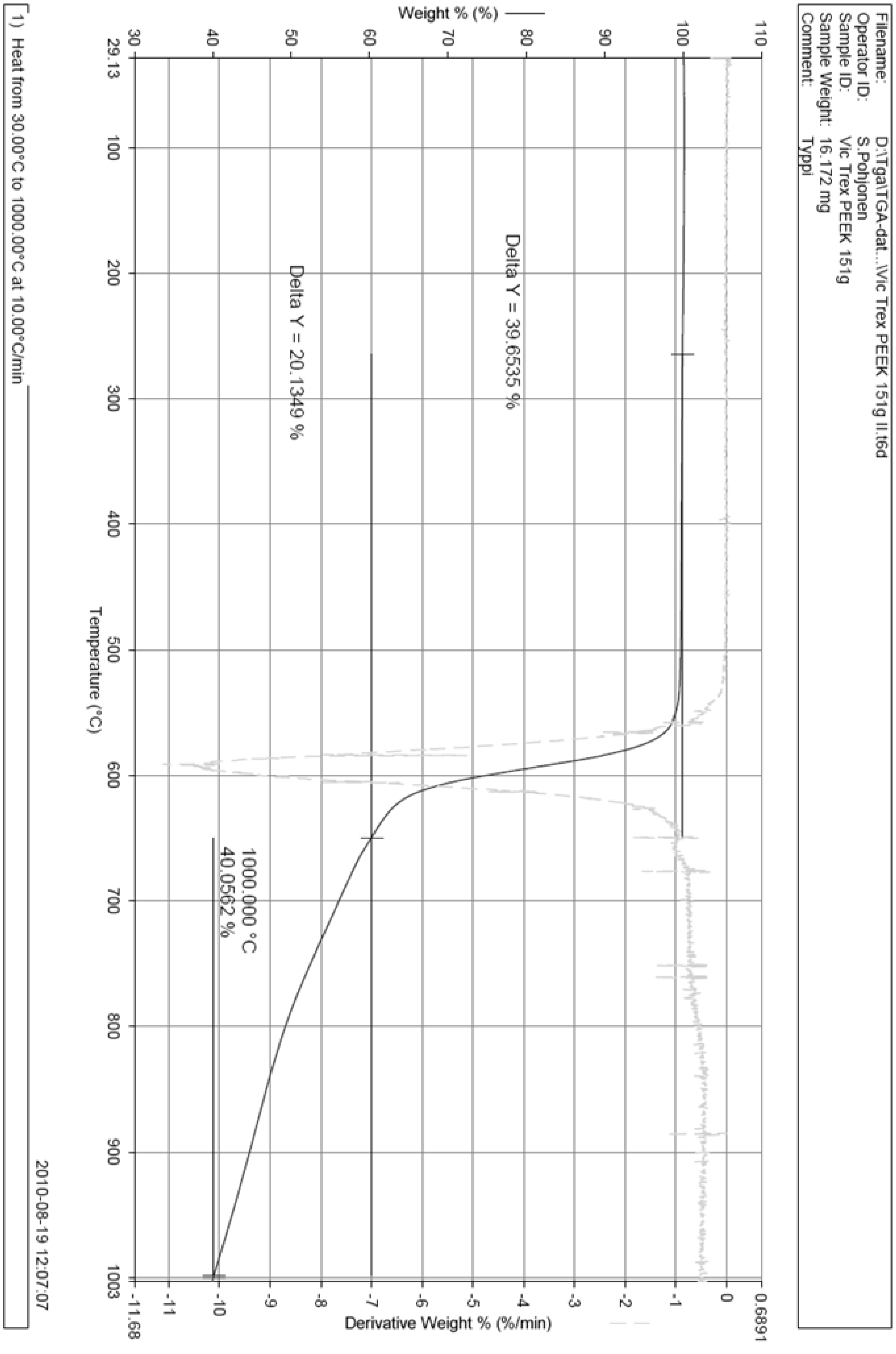
Project :
Identity : sulfonated
Date/time : 2011-01-11 12:56:43
Laboratory : Muovi- ja elastomeeritekniikk
Operator : S.Pohjonen
Sample : sulfonated, 9.820 mg

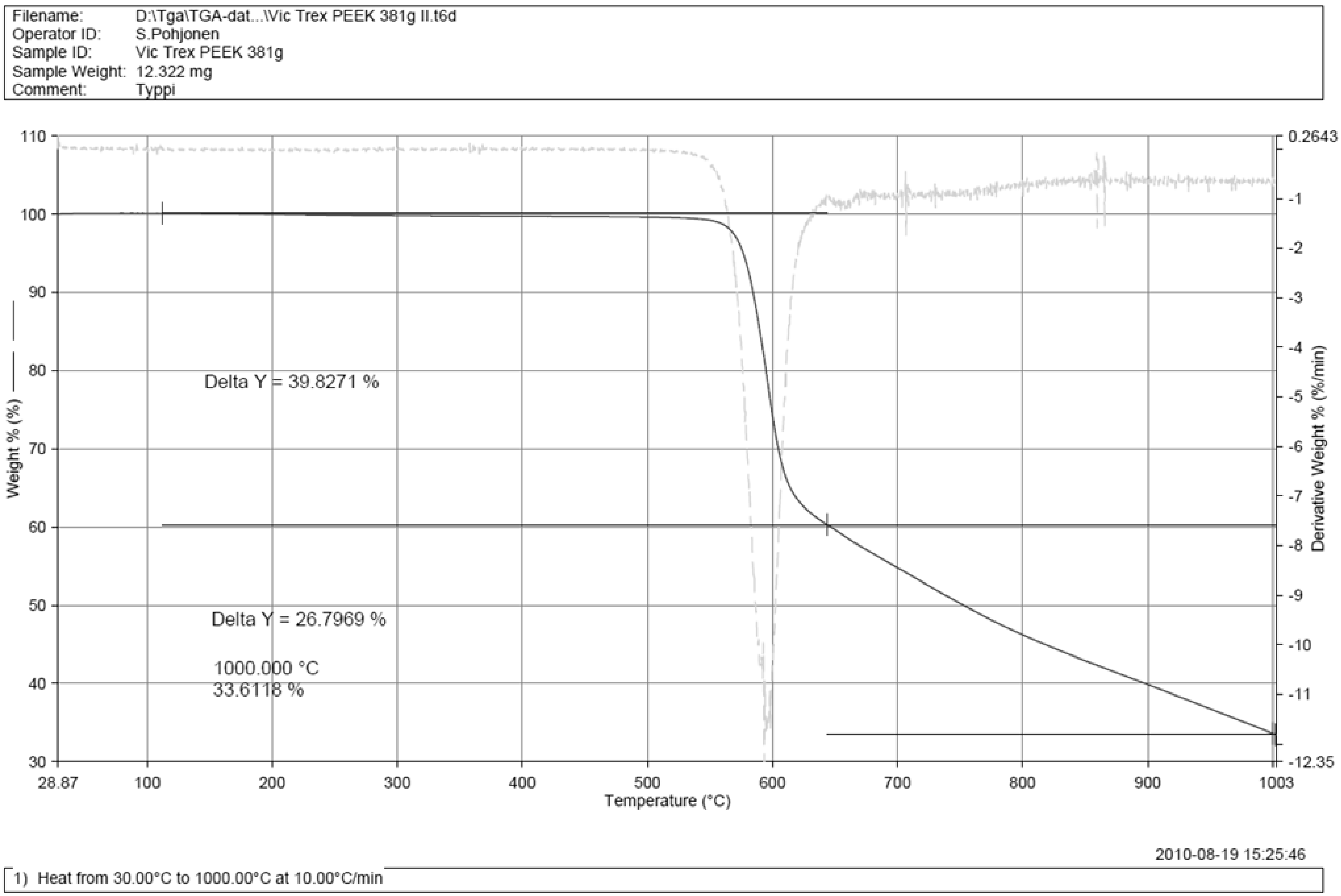
Reference :
Material :
Corr./temp.cal : / 250809-sen-pierced al pan-N2-10kpermin-fullcalib.td3
Sens.file : 250809-sen-pierced al pan-N2-10kpermin-fullcalib.ed3
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / Sample

Segments : 6
Crucible : Pan Al, pierced lid
Atmosphere : N2, 20.0ml/min / N2, 50.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	Co	P2:N2	PG:N2	LN2	GN2	Corr.
[3.3] Dynamic	0/20.0(K/min)/220	300.00	1	0	20.0	50.0	Off	Off	---
[3.4] Dynamic	220/20.0(K/min)/0	200.00	1	0	20.0	50.0	Off	2.0	---
[3.6] Dynamic	0/20.0(K/min)/220	200.00	1	0	20.0	50.0	Off	Off	---

APPENDIX 3: TGA-CURVES OF PEEK

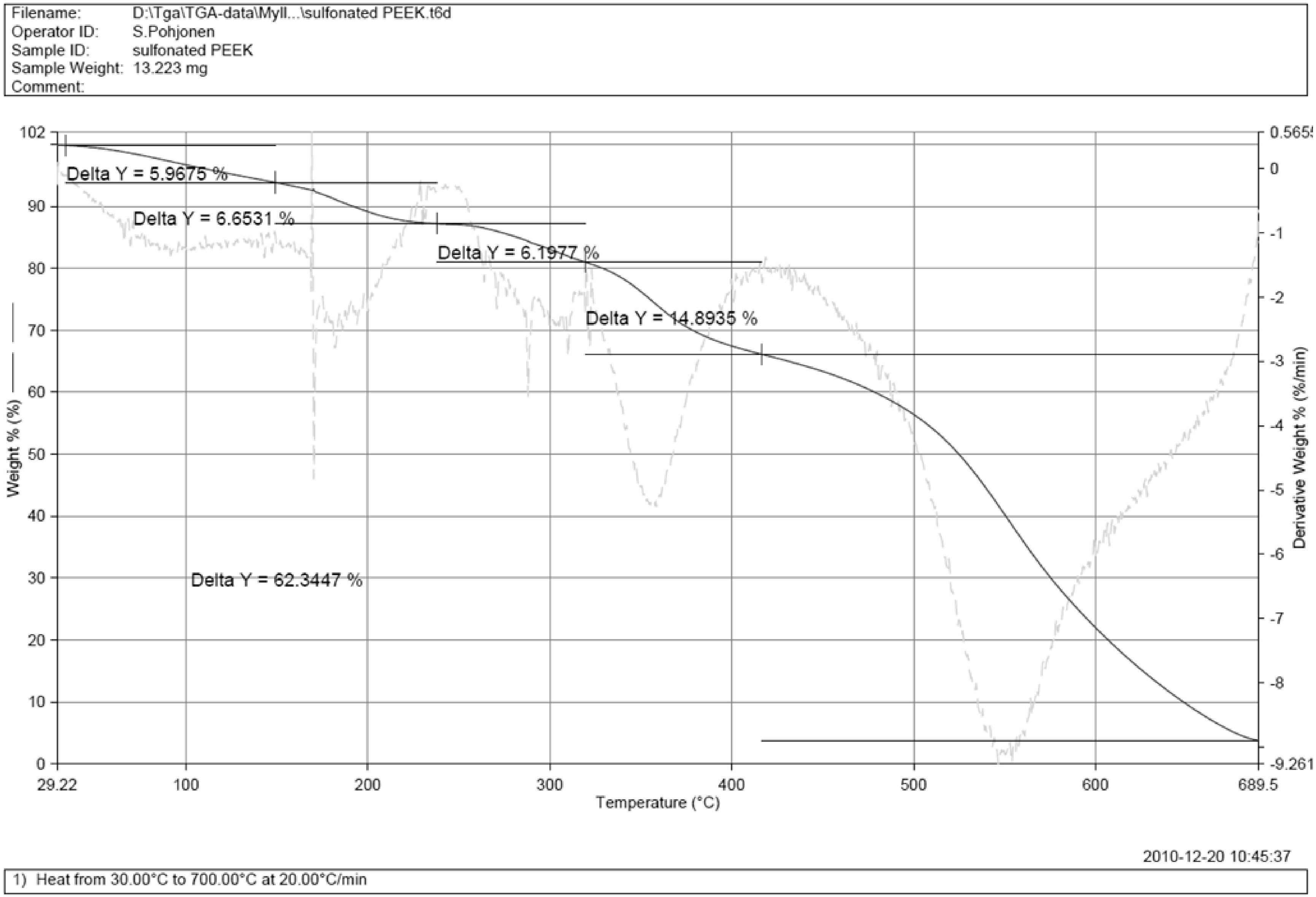




Filename: D:\Tga\TGA-dat...\Vic Trex PEEK 381g II.t6d
Operator ID: S.Pohjonen
Sample ID: Vic Trex PEEK 381g
Sample Weight: 12.322 mg
Comment: Typpi

2010-08-19 15:25:46

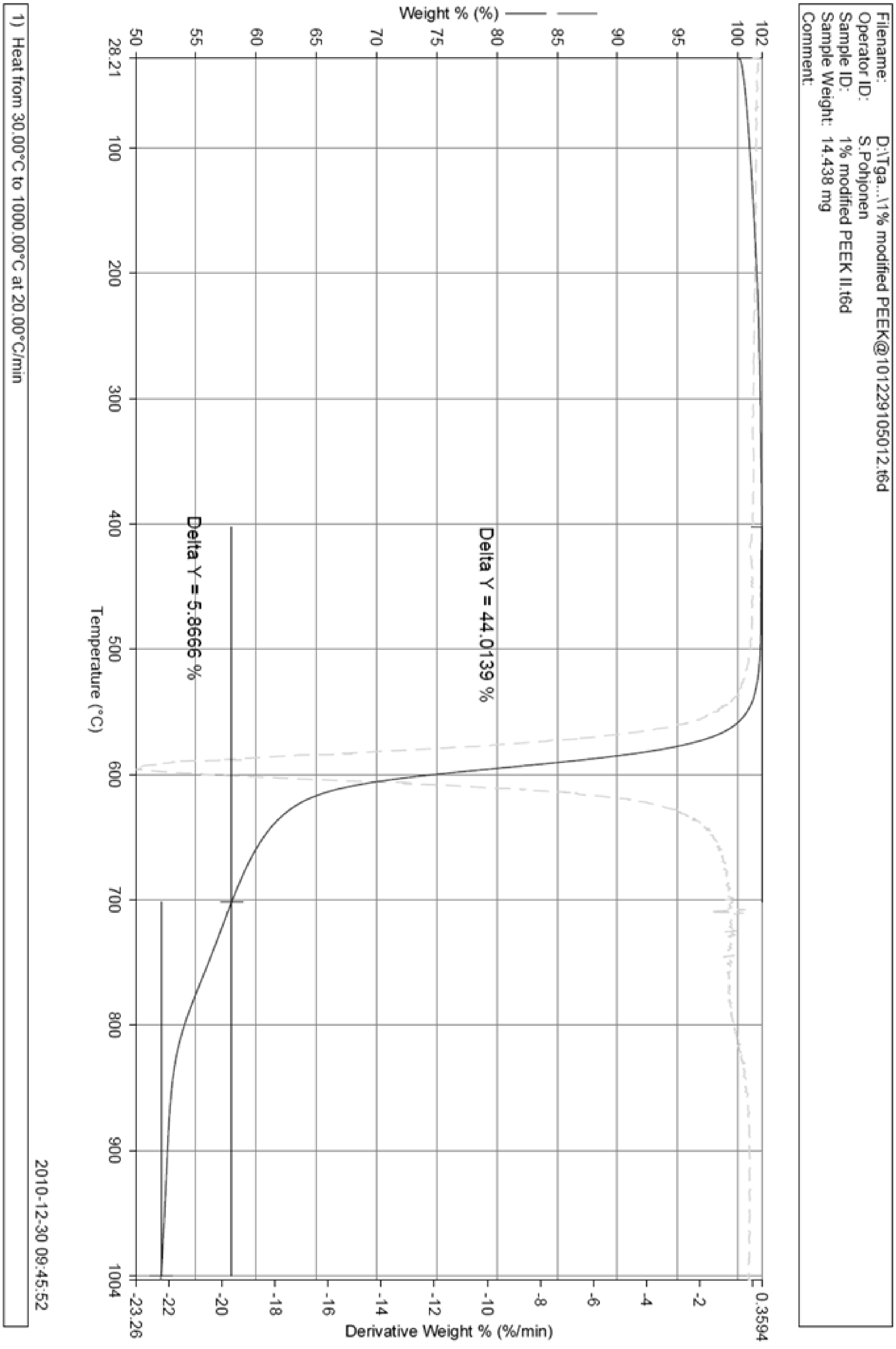
1) Heat from 30.00°C to 1000.00°C at 10.00°C/min



Filename: D:\Tga\TGA-data\Myll...\sulfonated PEEK.t6d
Operator ID: S.Pohjonen
Sample ID: sulfonated PEEK
Sample Weight: 13.223 mg
Comment:

2010-12-20 10:45:37

1) Heat from 30.00°C to 700.00°C at 20.00°C/min

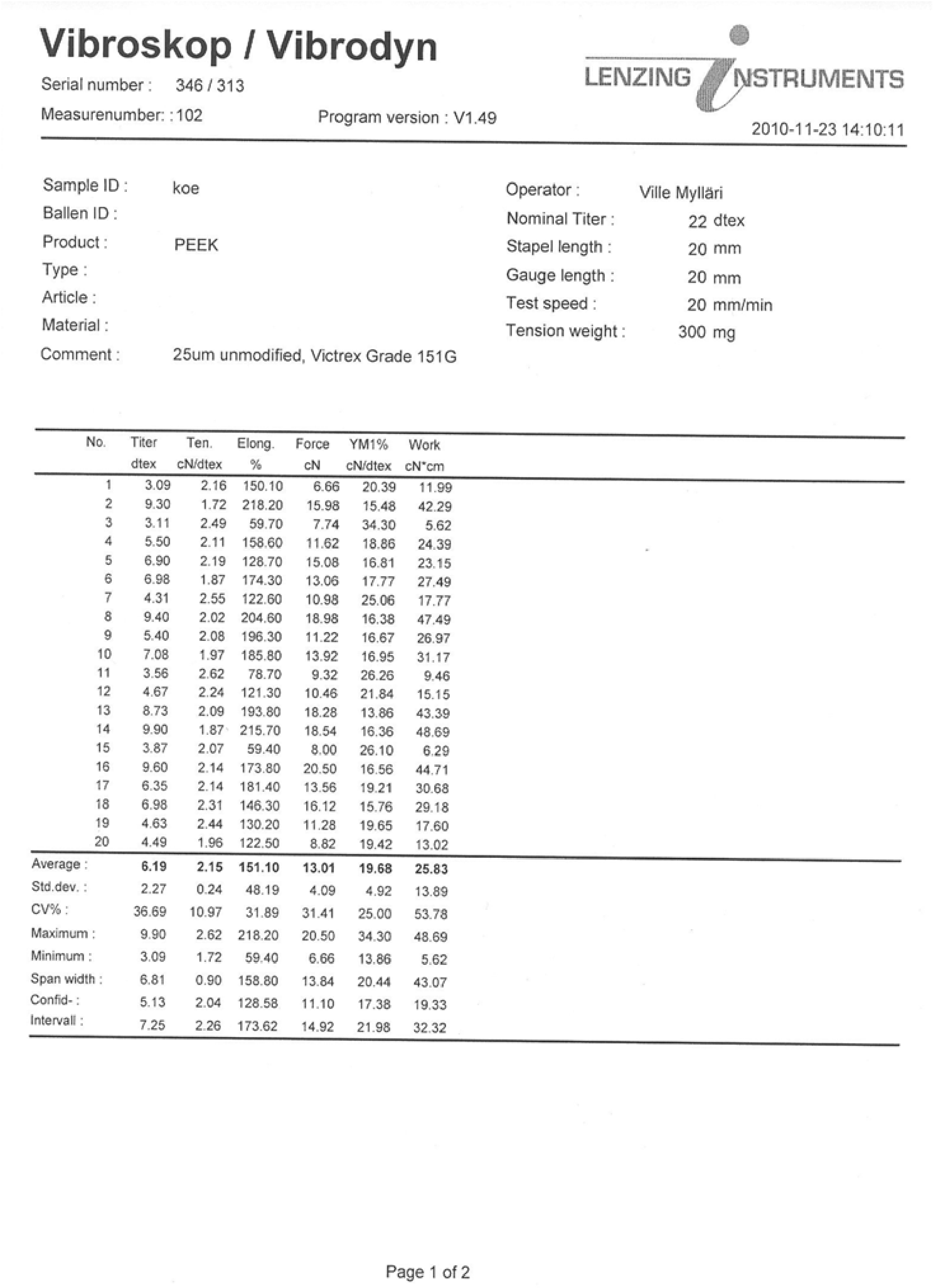


Filename: D:\Tga...\1% modified PEEK@101229105012.t6d
Operator ID: S.Pohjonen
Sample ID: 1% modified PEEK II.t6d
Sample Weight: 14.438 mg
Comment:

1) Heat from 30.00°C to 1000.00°C at 20.00°C/min

2010-12-30 09:45:52

APPENDIX 4: TEST DIARY OF MECHANICAL TESTS



Vibroskop / Vibrodyn

LENZING INSTRUMENTS

Serial number : 346 / 313

Measurenumber: :102

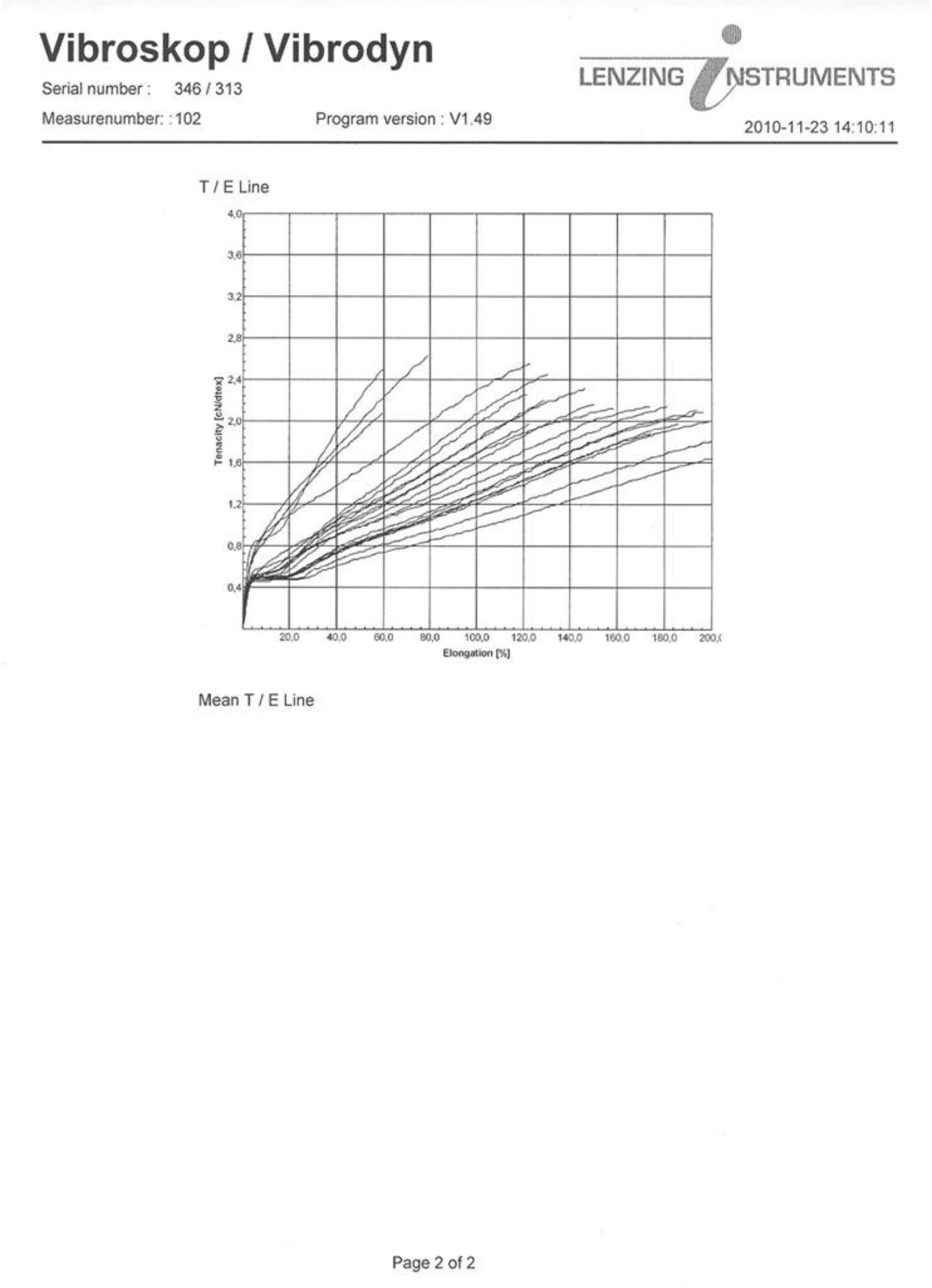
Program version : V1.49

2010-11-23 14:10:11

Sample ID :	koe	Operator :	Ville Mylläri
Ballen ID :		Nominal Titer :	22 dtex
Product :	PEEK	Stapel length :	20 mm
Type :		Gauge length :	20 mm
Article :		Test speed :	20 mm/min
Material :		Tension weight :	300 mg
Comment :	25um unmodified, Victrex Grade 151G		

No.	Titer dtex	Ten. cN/dtex	Elong. %	Force cN	YM1% cN/dtex	Work cN*cm
1	3.09	2.16	150.10	6.66	20.39	11.99
2	9.30	1.72	218.20	15.98	15.48	42.29
3	3.11	2.49	59.70	7.74	34.30	5.62
4	5.50	2.11	158.60	11.62	18.86	24.39
5	6.90	2.19	128.70	15.08	16.81	23.15
6	6.98	1.87	174.30	13.06	17.77	27.49
7	4.31	2.55	122.60	10.98	25.06	17.77
8	9.40	2.02	204.60	18.98	16.38	47.49
9	5.40	2.08	196.30	11.22	16.67	26.97
10	7.08	1.97	185.80	13.92	16.95	31.17
11	3.56	2.62	78.70	9.32	26.26	9.46
12	4.67	2.24	121.30	10.46	21.84	15.15
13	8.73	2.09	193.80	18.28	13.86	43.39
14	9.90	1.87	215.70	18.54	16.36	48.69
15	3.87	2.07	59.40	8.00	26.10	6.29
16	9.60	2.14	173.80	20.50	16.56	44.71
17	6.35	2.14	181.40	13.56	19.21	30.68
18	6.98	2.31	146.30	16.12	15.76	29.18
19	4.63	2.44	130.20	11.28	19.65	17.60
20	4.49	1.96	122.50	8.82	19.42	13.02
Average :	**6.19**	**2.15**	**151.10**	**13.01**	**19.68**	**25.83**
Std.dev. :	2.27	0.24	48.19	4.09	4.92	13.89
CV% :	36.69	10.97	31.89	31.41	25.00	53.78
Maximum :	9.90	2.62	218.20	20.50	34.30	48.69
Minimum :	3.09	1.72	59.40	6.66	13.86	5.62
Span width :	6.81	0.90	158.80	13.84	20.44	43.07
Confid- :	5.13	2.04	128.58	11.10	17.38	19.33
Intervall :	7.25	2.26	173.62	14.92	21.98	32.32

Page 1 of 2



Vibroskop / Vibrodyn

LENZING INSTRUMENTS

Serial number : 346 / 313

Measurenumber: : 102

Program version : V1.49

2010-11-23 14:10:11

T / E Line

Mean T / E Line

Page 2 of 2