Polymer Melt Wall Slip as a Phenomena Perversely Affecting Capillary Viscosity Data Evaluation

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Zásady pro vypracování:

V rámci řešené problematiky bude vypracována literární rešerše na téma skluzu polymerní taveniny při charakterizaci tokových vlastností. Blíže bude diskutován vliv použité experimentální techniky, typu testovaných polymerních materiálů a zkušebních podmínek. V experimentální části bakalářské práce bude skluz polymerních tavenin vybraných typů polyolefinů popsán pomocí kapilárního viskozimetru a získané výsledky budou vyhodnoceny s ohledem na aplikační potenciál použitého zařízení. Práce bude vypracována v anglickém jazyce.

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Forma zpracování bakalářské práce: **tištěná/elektronická**

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1) Smillo F., Wall Slip and Spurt of Molten Polymer, Master Thesis.McGill University. Canada. 2004
2) Shaw M. T., Introduction to Polymer Rheology, Hoboken: John Wiley & Sons, 2011

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ABSTRAKT

Cílem bakalářské práce bylo představit roli viskozitních měření polymerních tavenin pro popis jejich tokového chování a spolu s nastíněním možností evaluace viskozitních dat pomocí dostupných experimentálních zařízení identifikovat možné problémy projevující se v podobě tokových nestabilit. Za zvolenou a sledovanou nestabilitu toku polymerních tavenin byl vybrán skluz na stěně, který je možno u některých materiálů pozorovat např. v projevech tzv. „slip-stick“ chování, kdy se přilnavost molekuly k povrchu střídá s jejím utržením a dochází tak ke vzniku krátkodobého skluzu na stěně, což se na materiálu opouštějícím ústí kapiláry projevuje jako více či méně pravidelná povrchová porucha. V neposlední řadě je zde prezentována a diskutována možnost využití tokových vlastností polymerních materiálů v podobě bez nebo s aplikací různých korekcí toku, např. pro účely modelování technologických procesů, kdy použití nekorigovaných hodnot viskozity může být důvodem špatného designu zpracovatelského zařízení způsobující následnou nestabilitu výroby.

Teoretické představení možného vyhodnocení viskozitních dat bylo v praktické části bakalářské práce ověřeno pomocí popisu tokového chování vybraných polymerních tavenin. Pro jejich charakterizaci bylo využito vysokotlakého kapilárního viskozimetru Goettfert Rheograph 50. Experimentální charakterizace byla provedena s ohledem na vznik a průběh tokových nestabilit zapříčiněných skluzem polymerní taveniny na stěně kapiláry. Projevující se poruchy adhezních a kohezních sil působících na rozhraní polymerní taveniny a povrchu kapiláry, a negativně ovlivňující výsledky experimentálního stanovení smykové i elongační viskozity – skluzu na stěně – byly sledovány pomocí Mooneyho korekce. Jeho evaluace byla představena na třech různých polyolefinických materiálech – vysoko-hustotním polyetylenu (HDPE), nízko-hustotním polyetylenu (LDPE) a lineárním nízko-hustotním polyetylenu (LLDPE), jako typických zástupcích polymerních tavenin, jejichž makromolekulární struktura podporuje či potlačuje tendenci ke skluzu. Pro určení smykové viskozity byly použity dva módy měření dostupné na kapilárním viskozimetru – měření při kontrolované rychlosti smykové deformace a při kontrolovaném tlaku, a tyto byly srovnány.

Klíčová slova: **smyková viskozita, skluz na stěně, kapilární viskozimetr, polymerní tavenina**

ABSTRACT

Introduction of the role of polymer melts viscosity measurements for the flow behaviour characterization as well as outline of the possibility to evaluate viscosity data with regard of presentation of accessible experimental devices and identification of potential problems demonstrated in the form of flow instabilities, was the main target of presented Bachelor´s thesis. The wall slip was chosen as flow instability of polymer melt, which is possible to observe for certain materials as phenomenon inherence of so-called “slip-stick” behaviour, when the molecular adhesiveness at surface alternates with its desorption causing the short-term wall slip connected with more or less periodic surface failures of the material leaving the capillary exit. Finally the possible utilisation of the knowledge of polymer materials flow behaviour is presented and discussed in the form without and with different flow correction, for example for modelling of technology processes purposes, when application of apparent uncorrected viscosity values could be the reason of wrong design of processing device causing resulting production instability.

Theoretic presentation of viscosity data evaluation was verified in practical part of the Bachelor theses using selected polymer melts flow behaviour description. Their characterization was carried out employing high-pressure capillary viscometer Goettfert Rheograph 50. Experimental setup was implemented concerning the onset and development of flow instabilities caused by polymer melt slip on the capillary wall. Attending failures of adhesive and cohesive forces on the polymer melt and capillary surface interface negatively affects results of experimental evaluation of shear and elongational viscosities – wall slip – was determined via Mooney correction. Its evaluation was presented on three various types of polyolefin materials – high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE), as typical representatives of polymer melts having molecular structure promoting or suppressing the tendency to slip. Two measuring modes available on the capillary rheometer used were applied in order to determine shear viscosity – controlled shear rate and controlled pressure and these were compared.

Key words: **shear viscosity, wall slip, capillary rheometer, polymer melt**

"Education is not the learning of facts, but the training of the mind to think."

Albert Einstein

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My thanks belong to all who were my daily motivation, mainly to those who know that it belongs to them. Special thanks to my supervisor doc. Ing. Tomáš Sedláček, Ph.D. for his infinite patience as well as his support.

I hereby declare that the print version of my Bachelor's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

CONTENTS

INTRODUCTION

As the first mention of rheology can be considered the statement of Greek philosopher Heraclitus, who said 2 500 years ago that everything flows *(= panta rhei)*. Nowadays it is known that flow properties are relevant in terms of physical properties hereupon the branch of science dealing with the flow and deformation of the substance is called rheology. Rheology was defined in 1929 as “the science of deformation and flow of matter” by E.C. Bingham and M. Reiner [1].

Rheology provides to find out variations of the material properties such as elasticity and viscosity with respect to applied stresses. Physical properties of liquids and solids, describing rheological properties including as for example strain, strain rate, elasticity moduli, and viscosity could be characterized via suitable rheological apparatuses and measuring methods. The basic condition of appropriate rheological measurement is the ability to measure force, distance and time [2]. In addition, since rheology could be utilized for more detailed polymers characterization as method with fine susceptibility to small changes in polymer structure, it can be employed as a useful tool for new materials investigation. A compelling reason for studying rheology and rheological properties of materials could be seen in evaluation of flow behaviour in context of real processing situations [3].

Conventional rheological models used for flow behaviour description is shown in *Figure 1*, where pure shear deformation is presented on material element, deemed thin liquid layer, dividing two plates by distance h *(m)*. The lower plate which has a surface area A *(m^2)* is stationary against the upper plate, which is moved by a force F *(N)* at a speed v *(m/s)*. While shear stress τ *(Pa)* is the tangential force F acting on area A to effect a movement in the liquid, shear viscosity

$$\eta = \frac{\tau}{\dot{\gamma}} \quad \textit{(Pa.s)} \qquad (1)$$

is the proportionality constant between shear stress and shear rate, where shear rate corresponds to the change of shear strain

$$\dot{\gamma} = \frac{\mathrm{d}x}{h} \quad \textit{(dimensionless)} \qquad (2)$$

with respect to time as the deformation resulting from tangential force. It is important in rheological measurement to achieve laminar flow whereas turbulent flow causes undesirable instabilities of the measured flow resistance.

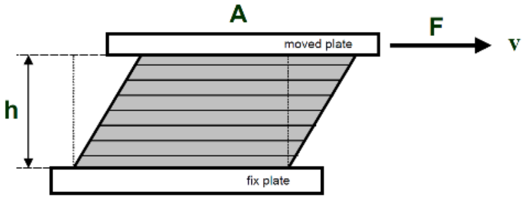


Figure 1: Parallel plate model [4].

While moving plate is typical for viscosity evaluation via torsion rheometry for example with plate-plate geometry, as it will be describe further in the text, capillary rheometry measurements could be described via velocity profile in capillary tube, which is depicted in *Figure 2.*

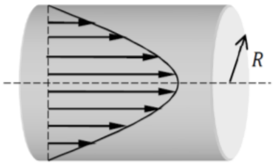


Figure 2: Velocity field in pressure driven tube [4].

It is well known, that shear stress is generated between two nearby layers of liquid, like material moving with different velocities as it is graphically presented through the velocity profile with assumed zero velocity at the wall of capillary and maximal in the middle. The shear stress value is assumed to be proportional to the difference of these velocities and flow resistivity expressed with Newton´s viscosity law.

I. THEORETICAL PART

1 VISCOSITY OF POLYMER MELTS

1.1 Polymer melts

Polymers melts could be described as viscoelastic fluids, which behaviour is manifested more or less viscous or elastic in dependence of velocity of its flow or how fast it is deformed during the process.

In the melt, the material is not only above its glass transition but also the flow temperature which means it is no more tough as in the solid state but it is modular and viscous. As the fluid is considered “a substance that alters its shape in response to any force however small” and generally it is continuously deformed under the effect of shear stress [1]. Thus for characterization of polymer melts properties, rheology, as a tool dealing with issue of solving viscoelastic problems concerned with that in liquid state, should be used. It is useful to take into account the inability of polymer melt of the energy storage which is invested in the form of stress as well as the incompressibility of the fluid.

Polymer melts are subjected to stress relaxation (see *Figure 3*) giving them unusual behaviour, which exactly means that materials relax in time and induced stress decreases in response to the same amount of applied strain [1]. Overlapping and branching of molecule chains are the main feature of the polymer melts enabling their mutual entanglement and thus affecting their elastic behaviour (chains entangled together are after termination of stress applying pushed back into their original state). This is also the reason why it is considered about polymers memory of its deformation history [1].

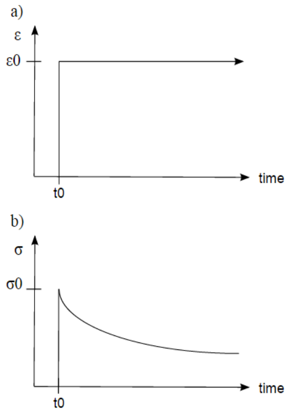


Figure 3: Stress relaxation

1.2 Viscosity

Material´s response to deformation could divides them into three groups of different properties – the elastic materials such as metals; the Newtonian fluids like air, water, gasoline and liquid metals; and the non-Newtonian fluids including polymeric fluids and for example human blood.

Pure elastic materials which are not a subject of this thesis, are described by Hooke´s law:

$$\tau_e = G \cdot \gamma \tag{3}$$

Where τ_e represents elastic shear stress, γ – shear strain, G – shear modulus (or E – Young´s modulus for tension). Elasticity, as a mechanical property, gives the possibility of material to deposit elastic energy into the substance during the deformation whereupon after termination of applying stress it is utilized due to relaxation and regeneration of its original shape. That impart to elastomers high level of elastic deformation.

Newtonian fluid presents rheological model of viscous matter, as it is shown in *Figure 4* [1]. Viscosity of Newtonian fluid η, as a material constant describing the toughness of a material or actually the resistance to flow, does not depend on the shear rate nor on the time flow as was defined above such as Newtonian law. This equation is valid for systems, named by Isaac Newton, like gases and liquids, which are formed by molecules with molecular weight less than about 1000 [5]. Since the energy of deformation of viscous system is completely dissipated in material, recoverable strain is equal to zero value [4].

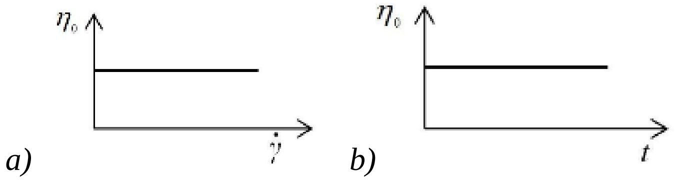


Figure 4: Viscosity of Newton´s substances such as quantity independent: a) on the shear rate, b) on the time

Table 1 illustrates selected substances and their corresponding shear viscosities at temperature of 20°C in *Pa.s.*

Table 1: Selected substances with shear viscosities at 20°C.

Substance	**Viscosity η [*Pa.s*]**
Acetone	$0{,}3.10^{-3}$
Water	$1{,}0.10^{-3}$
Ethanol	$1{,}2.10^{-3}$
Honey	1.10^{2}
Polymer melts	1.10^{1} - 10^{6}

The *Figure 5* shows differences between dependences of viscosity for Newtonian and non-Newtonian cases. While for Newtonian fluids it does not matter, in term of rheology, how fast and how much force is applied on material seeing that their viscosity is independent of time and shear rate, non-Newtonian matter does not subject to Newtonian behaviour. In the case of non-Newtonian fluids the dependence between viscosity and applied speed exists as well as between viscosity and pressure which affects them to flow. As the speed (shear rate) increases, the viscosity of non-Newtonian fluids decreases, while the Newtonian one remains constant. Viscoelasticity is taken as the reason of time dependent stress-strain behaviour. After termination of the applying stress, molecules need the relaxation time to achieve the energetically most advantageous state given by characteristics of the polymer chains [4].

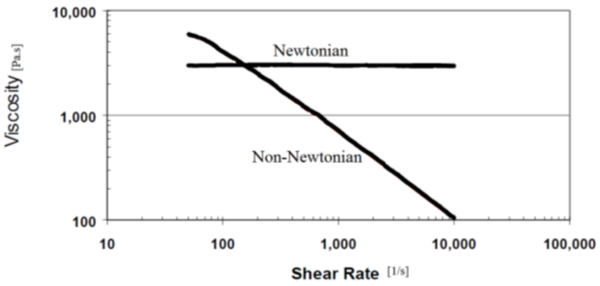


Figure 5: Newtonian simple shear rate/viscosity curves vs. non-Newtonian one

While shear viscosity of Newtonian fluids is obtained from the slope of shear stress versus shear rate, for non-Newtonian fluids it is defined as a function of apparent shear rate, uncorrected to various exhibitions of viscoelasticity, as it will be described further in the text. Typical representatives of the third mentioned material type, non-Newtonian fluids, are polymer solutions and melts, consisting of very large molecules (made up by repetition of chemical units) with the molecular weights about 10^5 - 10^8 [5]. Macromolecules length is the true essence of non-Newtonian behaviour since they are long enough to entangle between each other thus affect themselves mutually. Moreover, the macromolecular structure, whether linear or branched, is another important parameter influencing the material viscoelastic properties. In other words it means, that free motion of the molecule chains, strongly depends on presence of long branches or large groups as the benzene ring, connected to backbone of molecular chains.

Flow characterization of polymer materials is described by using the flow curve, which is given by relation between viscosity and a shear rate. *Figure 6* demonstrates the flow curve of polymer material, where in the first *part A* Newtonian behaviour occurs just in the small interval of shear rate values. In the next *part B* where the viscosity ceases to be independent of shear rate and with polymer materials decreases, then in the *part C* the depending directive is gradually stabilizing up in *part D*, called the second Newtonian plateau, which is characterized by steady state of viscosity as the quantity again independent of shear rate because of its complicated measurability [6].

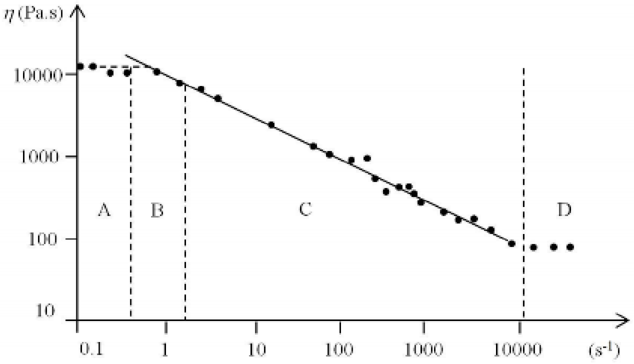


Figure 6: Flow curve of polymer material [6].

Since at molecular level variations in molecular vibrations with temperature and pressure changes could be observed, beside shear rate also temperature and pressure need to be taken into account. As Brownian motion of the chains rises, easier flow (of polymer melt) is enabled and viscosity decreases, vice versa restriction of Brownian motion causes viscosity increase. Due to this fact the viscosity of fluids is significantly affected by the processing conditions, namely it exponentially decreases with temperature and increases with pressure [1, 2, 4]. Temperature effect on the viscosity behaviour for non-Newtonian case is presented in *Figure 7.*

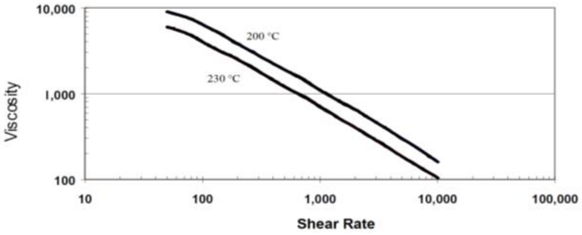


Figure 7: Simple shear rate/viscosity curves at two different temperatures.

Moreover the fact, that flow behaviour of polymer melt is not simple shear stressed, but also elongated, the shear and the elongational flow, described by shear or elongational viscosity, respectively, should be distinguished. Nevertheless both of them permeate each other during the real flow process conditions additionally substantially affected by pressure and temperature [7].

Finally it could be mentioned, that pure polymer materials are often modified with various additives. In general, polymer additives are added into polymeric materials in order to improve their properties in connection with their processing or further utilization. There are lots of different types with various purposes as for example manufacturing or processing additives, antidegradants like heat and UV stabilizers, special additives for hydrophobicity/hydrophilicity modification, slipping agents and many others affecting target physical properties of polymers. Moreover as polymer additives could be considered also powdery or fibrous substances such as carbon particles, kaolin or fiberglass most often used for modification of mechanical properties of material. While added ingredients commonly affect properties of the final product as climatic resistance, appearance of surface, thermal or light stability, it should be kept in mind that their addition also changes processability of modified materials in many ways. Viscosity could be increased in the case of highly filled materials, processing stability could be increased after addition of thermal stabilizers or manufacturing with increase effectiveness could be reached by addition of processing aids [8].

1.3 Polymer melt elongational viscosity measurement

Elongational, also called extensional viscosity, η_E, corresponds to the resistance of polymer melt against extensional stress, could be defined as

$$\eta_E = \frac{\tau}{\dot{\varepsilon}} = \frac{\frac{F}{A}}{\dot{\varepsilon}} \tag{4}$$

In general, it is increased with molecular weight and for polymer melts it lies in the range about 10-100 times larger than the shear viscosity, especially for branched polymers in the region of low to middle strain rates due to entanglements and interconnection of branching points. Practical applications are important in processes where high elongation rates could be expected as for example injection molding or extrusion characterized with free surface deformation (fibres and foam preparations, film blowing, etc.).

It is possible to measure extensional viscosity on the extensional rheometers, as for example Munsted type, which however does not allow evaluation of elongational flows at high extensional rates. In contrast high strain rate viscosity evaluation could be carried out employing capillary rheometers. While in this case there is problem related with absence of homogenous extensional flow during measurement, after application of basic corrections measured capillary viscosity data could be evaluated by the help of a suitable models proposed for example by Cogswel and acceptable results could be achieved [7].

1.4 Polymer melt shear viscosity measurement

As it was mentioned before, rheology of polymer melts is greatly influenced by molecular parameters as mean molecular weight, molecular weight distribution and branching of the molecular chains. Even the small changes of all this structural properties probably cause the changes in global rheology properties of the polymer melt. Due to this fact, degradation of polymer melt induced due to moisture absorption by polar polymer chains in connection with air humidity significantly effects viscosity measurements as well as impurities in polymer sample caused by improper blend or fillers mixing. Moreover thermal inhomogeneity will induce the crucial problems during viscosity behaviour measurements similarly to insufficient thermal stability of tested materials due to impressing thermal degradation or cross-linking [3, 4]. In general, there are two types of shear rheology measurement namely based on drag-flow and pressure driven-flow. Drag flow is observed with rotational rheometers which allow determination of viscometric and viscoelastic functions of polymer melts. To measure a correct pressure driven-flow viscosity data, utilizing capillary rheometer, it is necessary apply many corrections concerning non-Newtonian behaviour of polymer melts. Among casually used methods, not only in this work, belong Rabinowitsch correction, Mooney correction and the Bagley correction.

1.4.1 Rotational rheometry

Rotational rheometers for evaluation of rheological properties of polymer melts are equipped with cone-plate or parallel-plate geometries. It is based on rotating or oscillation of circular plate-shaped sample between the upper and lower part of geometry. The scheme of cone-plate and parallel plate geometries can be closer seen in *Figure 8*. In the most cases a lower part of geometry is stably fixed whereas the upper part is rotational moved.

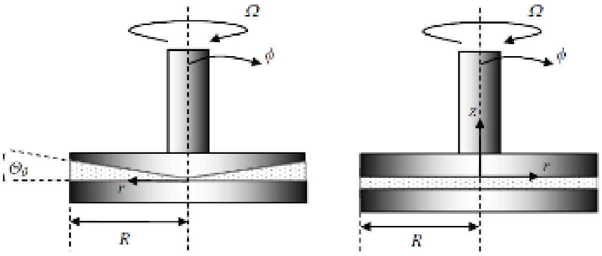


Figure 8: Cone-plate (left hand side) and parallel-plate (right hand side) rheometer geometries [4].

Utilization of the cone-plate rheometer found application also in evaluation of non-linear properties at small deformation rates. Since shear rate depends on angular velocity as well as on the thickness and radius of the sample when the parallel-plate rheometer is employed, only limited strain is possible to be applied for viscosity behaviour description. Different shear rate distribution could be noticed, becoming zero in the centre and the highest on the edges of tested sample [4]. In other words, it should be highlighted that while effects of temperature could be easily checked using rotational rheometers, low to moderate region of shear rates is one limitation, evaluation of pressure effects is the other.

1.4.2 Sliding plate

Sliding plate rheometer, shown in *Figure 9*, could be very useful for drag-flow measurements under the various process conditions including strain-rate, temperature and pressure. A distinct advantage is the possibility of operating at both high pressures and shear rates during the measurements. As opposed to rotational rheometers using plate-plate geometry it is not necessary to worry about the round shape of the sample and the associated problems with the edge effects causing viscosity deviations, just because of scanning the shear stress in the middle of a sample. Moreover, geometry construction gives the possibility of generating steady flow without any pressure gradient. Nevertheless, the important downside can be considered in connection with commercial unavailability [9, 10].

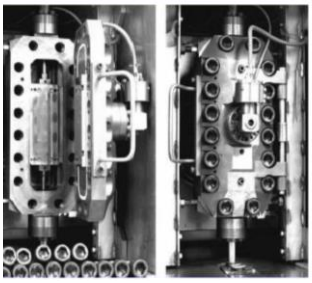


Figure 9: Photo of High-pressure sliding-plate rheometer: (left) cover plate open; (right) cover plate closed [9].

1.4.3 Capillary rheometry

Capillary rheometry is the most often used device for melt viscosity measurements. Compare to rotational rheometry, capillary rheometers enables at various temperature conditions viscosity determination in the moderate-high shear rate flow region which is more useful and also closer to real processing situations. For evaluation of pressure-driven flows various geometries such as pipes, extrusion dies, slit die geometry or a round-hole capillary as was used in this work [4, 10] are available. Moreover there are several types of capillary rheometers differing in number of barrels, way of pressure generation (compressed gas, gravity or piston) or measured quantity (controlled-pressure and controlled-rate mode) [7].

As it can be seen in *Figure* 9, capillary rheometer is composed of the rod, used as a piston leading to the barrel, inducing a pressure affecting the sample melted in a pre-heated reservoir of known radius and dimension. The following part of the system is formed by the constricted portion called capillary tube, which is accessible in many variations of different lengths and radii. In the way from barrel to outside of capillary is placed the pressure transducer for evaluation of pressure drop between enter and exit of capillary. Moreover also a temperature sensor for continual scanning of temperature value could be employed.

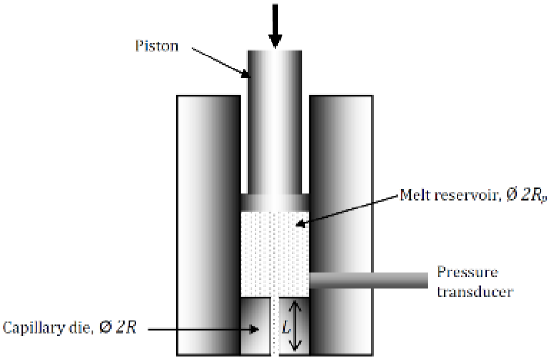


Figure 10: Principle of the capillary rheometer [4].

The calculation of viscosity is based on the measured raw pressure and velocity data, which give the apparent shear stress and apparent shear rate as seen in equations below:

$$\dot{\gamma}_A = \frac{4Q}{\pi R^3} \tag{5}$$

$$\tau_A = \frac{\Delta p}{2(\frac{L}{R})} \tag{6}$$

where Q means volumetric flow rate and Δp, R, L are applied pressure, die radius and die length [4]. When the polymer melt flows through a channel a laminar flow, described by Hagen-Poiseuille law could be observed for Newtonian fluids. It means that velocity is maximum at the centre but conversely the velocity gradient or shear rate and also shear strain get the highest value at the wall and zero in the centre of the flow [5]. While simple preconditions are assumed for the capillary data evaluation, as for example conclusively isothermal flow, incompressibility of the melt, insignificant pressure dependence of the viscosity, the melt sticks to the wall and steady shear flow [10], much more complex flow matches real flow conditions. In addition also the fact that polymer melts are non-Newtonian fluids will cause other complexity in connection with various values of velocity across each radial positions [2]. Consequently, several deviations, instabilities and complications like a wall slip, melt fracture, extrudate swell, entrance pressure drop and possibility of a material degradation during time spent in the reservoir need to be taken into account in order to get more realistic view of real polymer melt flow during its processing. To avoid an incorrect data evaluation it is necessary to applied several correction as it will be discussed further.

The first correction introduced for capillary measurement of polymeric liquids is the Rabinowitch correction, which is used to correct the shear rate values.

$$\dot{\gamma} = \frac{3n+1}{4n} \cdot \dot{\gamma}_A \tag{7}$$

where *n* is viscosity shear thinning exponent, proportional to decrease of shear stress with shear rate, defined as:

$$n = \frac{d \log \tau_W}{d \log \dot{\gamma}_A} \tag{8}$$

Secondly viscoelastic material flow gets complicated with pressure drop on capillary entry and exit causing a total pressure increase. Moreover, this pressure arise is steadily increasing with an applied shear rate growth. Definitely, this extra pressure drop is more significant at the entrance of the capillary compare to its exit. The reason is that the polymer melt, suddenly flowing from the wide reservoir through the narrow slit, requires increase of pressure due to flow disturbances occurring. Disturbances (as figured in *Figure 11)* represented by recirculating corners in the position of restriction, represented by the reservoir end and capillary beginning, observed in capillary flow are visible for material with high-molecular weight and elasticity [4], which could be explained via more significant entanglements in the case of these materials.

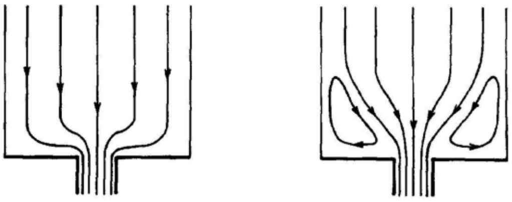


Figure 11: Streamlines in the Entrance Region of a Capillary for a linear (HDPE) and branched (LDPE) polymers [4].

For the calculation of the real shear stress free of measuring errors on capillary rheometer, there is necessary to employ the Bagley correction. It operates on the principle of repeating measurement at chosen shear rates with the capillaries having the same diameter and different lengths [4], as it is graphically presented in *Figure 12*. Or utilisation of the multi-piston rheometers offer to applied Bagley plot evaluation in parallel viscosity measurement utilizing capillaries of constant diameter *D* and different *L*/*D* ratio for determination of the entrance pressure in shorten time [2].

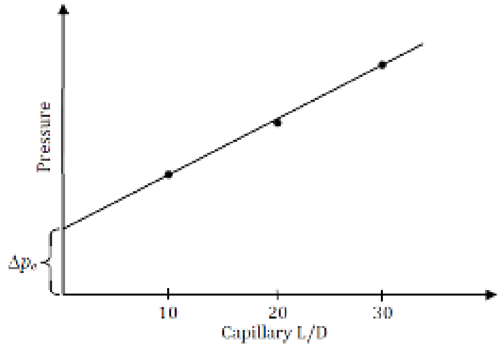


Figure 12: An example of Bagley plot with capillary length to diameter ratios 10, 20 and 30 at one measured shear rate [4].

Another possibility is to use the orifice capillary in complementary measurement to long capillary experiment. It means that employment of an almost zero length and a long capillaries could be used for direct determination of the entrance pressure [2], instead of the necessity to carry out the linear regression subtracted from the total pressure, the section on *y* (pressure) axis, appropriate the zero value length on *x* (*L*/*D*) axis. It should be mentioned that determination of the corrected shear stress given in *Equation 9*, or true rheological behaviour, via application of this correction is very important for real process simulation.

$$\tau_{W}= \frac{\Delta p-\Delta p_e}{2(\frac{L}{R})} \tag{9}$$

At the capillary determination of polymer properties can be looked such as a great first and relatively fast and simple test of a new material [5]. One of many advantages is that for capillary measurement is needed just a small amount of sample.

Finally, as the third important and known correction also Mooney correction should be introduced. The Mooney correction should be used, after successfully applying of the Bagley end correction to the raw measured data [2]. In this way the slip velocity of polymer melt on the capillary wall is determined, defining differences according to assumption that velocity on the wall is equal to zero. It is applied through the experiments where more than one capillary (usually at least three) with the same length to diameter ratio (*L/D*), nevertheless contrary to Bagley corrections with different radii in this case. Corrected shear rate – without wall slip effect - is determined for the specific shear stresses via extrapolation of shear rate to endless diameter from the dependence of wall shear rate on the radius [11], since rising diameter of the capillary descend the probability that the slip occurs – in other words the wall slip gets zero value when infinitely large capillary is used. No slip conditions are illustrated as flattened velocity profile with any chance to originate of marginal wall slip. *Figure 13* depicts Mooney plot of polymer melt which is measured with three different capillaries at various pressure values.

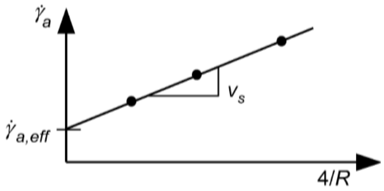


Figure 13: Mooney plot for a constant wall shear stress [10]

The biggest disadvantage of commercially available capillary rheometer is the way of pressure control during the measurement. There is a pressure transducer in the lower part of heated barrel which responds with 0.5% pressure tolerance and with a time lag. H. M. Laun introduced an automated gas driven capillary rheometer, where nitrogen is utilized for gas pressure driving of rheometer. On this special type of rheometer could be measured more accurately at imposed wall shear stress instead of other types working at imposed flow rate [10]. The instant response on the pressure changes enables an exact determination of wall slip velocities from Mooney plot.

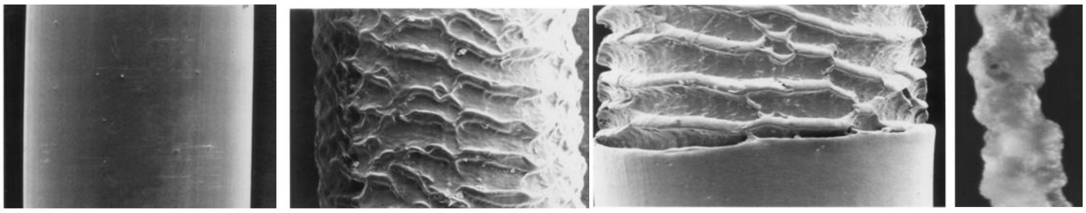
1.5 Capillary flow instabilities

It is known in nowadays polymer processing industry that resulting products are affected by flow instabilities proceeding due to its properties. The basic requirements to detect these polymer flow discrepancies is to carried out a complex rheological experiments, analogous to those used for description of flow behaviour of liquids, solids, metals and also rubbers. Extrudate distortions occur when high, respectively higher then critical, shear stress is applied on plastic materials during its processing causing the rough quality problem in final products, thus it is intensifies in the case when shear stress increases [12]. While, for presented study was chosen a wall slip as examined capillary flow instability, from among other instabilities should be named a melt oscillating fracture, sharkskin and stick-slip. A correction, applied on shear rate for instabilities in flow for non-Newtonian behaviour, pronounced as first Rabinowitsch.

Compared to a stable state shown in *Figure 14 a)* there are noticed pursued flow instabilities in *Figure 14 b)-d).* Sharkskin is observed as the first processing problem which is characterized by visible surface distortions running in periodic intervals.

Slip stick is appearing due to a pressure and flow rate oscillations, when rough and smooth surface of extrudate is changing [13].

Finally, gross melt fracture could be characterized by total loss of any surface smoothness or small symmetrical instabilities occurrence. This type of instabilities is typical for very high shear stresses and processing velocities.



a) b) c) d)

Figure 14: a) stable; b) sharkskin; c) slip-stick; d) gross melt fracture [14]

1.5.1 Wall slip

Although the slip is typical instability of filled polymers, attention is increasingly paid to this phenomenon for its importance as a frequent and common extrusion defect [12]. First time talked about the wall slip Mooney, who measured the flow curve with different capillaries [15]. Failure of adhesion and cohesion forces at the interface of the capillary surface and the adherent molecular monolayer is considered as the cause of the slip [12]. The slip velocity depends on the shear stress [11], thus to achieve the wall slip it is necessary get into the critical shear stresses which cause failure of the entanglement between molecules, easily in high molecular weight linear polymers [12]. This type of slip which is incurred by simply slipping of polymer melt over solid surface because of desorption the surface layer [16] due to adhesive failure depends not only on the used material but also on the geometry of used tool and its construction material [11]. Different additives thus present various impacts on development of flow instabilities, concrete the wall slip. While some of them could supress the possibility of onset of wall slip, the others one could causes continuous run of the slip.

Usually the zero velocity at the interface of the capillary surface and the molecular chain is observed. Loss of contact on this interface momentary causing setting of polymer melts slip on the wall [12]. The second possibility how the slip could be started is disentanglement of molecules away from the monolayer which is in continuous contact with surface [16], therefore caused by cohesive failure of the material as material´s property [11]. It means that the wall slip is represented by the fault in shear rate as it is presented in *Figure 15*, where the velocity profile affected by wall slip in a capillary is shown. It is assumed that among the factors affecting formation and progression of the wall slip belongs not only to the chemical structure, as for example branching of the polymer, but also external influences such as temperature or shape and material construction of the capillary [12].

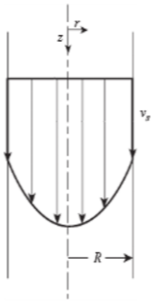


Figure 15: Velocity profile with wall slip in a capillary [11].

The smaller capillary diameters induce the sever slip effect. In other words, arise of the capillary diameter descends probability that the slip occurs – that means that the wall slip gets zero value when infinitely large capillary is used. It should be illustrated as flattened velocity profile with no chance to originate of marginal wall slip. It is evident from *Figure 16* that the wall slip velocity profile consists partially of the plug flow and the following partial slip part of velocity profile.

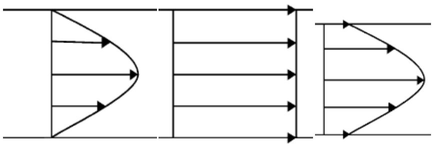


Figure 16: Typical velocity profiles of polymer melt flow in capillaries: (left) no-slip; (middle) plug flow; (right) partial slip [17].

Slip at the wall of the capillary could not be continuous and it can be observed in very short processing term characterized by temperature and amount of flow rate, in which the wall shear stress alternates between two states, when molecules of polymer melt are adhered or separated from the solid surface, is called the "slip-stick" behavior [7, 18].

1.5.2 Spurt and oscillatory flow

For measuring viscosity data by using capillary rheometer there are two possibilities how determine it, and the consequent kinds of flow instabilities – spurt and oscillatory flow. The first method is when piston speed is controlled, than the shear rate could be calculated from a defined and monitored speed and dimensions of reservoir and the second one with controlled pressure, which allows calculate shear rate from measured flow rate. If the specific pressure pushing the piston is set, than with the controlled pressure change becomes also sudden change in flow regime characterized with increasing volumetric flow rate manifesting as phenomena called spurt. Differently when piston speed is controlled there is observed not only volumetric flow but also pressure periodic oscillations occurring over a certain value of piston speed when extrudate alternates between smooth and rough surface manifestations [12]. In the *Figure 17* are illustrated common extrudate distorsions.

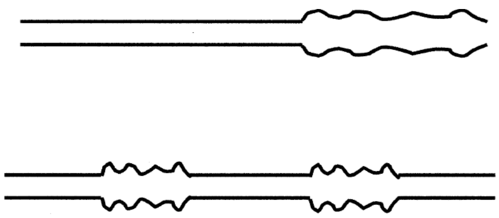


Figure 17: Top: spurt; bottom: oscillatory flow [12].

As a spurt flow was firstly named the stick-slip behavior by Vinogradov and coworkers however the stick-slip as flow instability is the subject of many other studies and experiments ant it is known by many different names (for example oscillating melt fracture or cork flow) [13].

II PRACTICAL PART

2 THESIS SCOPE AND OBJECTIVES

Introduction of the role of rheology in the polymer processing was the overal aim of presented thesis. Rheology was interpreted as tool enabling description of the polymeric materials flow during their manufacturing. Further it was introduced that flow characterisatin is often, in connection with polymers viscoelastic properties, complitated by the various processing instabilities as for examle slip. Moreover it was shown that these instabilities could be significantly affected not only by the change of polymer molecular structure and composition, but also by the presence of commonly used additives.

Since increase of the manufacturing processes effectivity is in general one of the main role of the technologiests and production engineers, description, determination and validation of process instablities were chosen as convenient experimental task of practical thesis part. In the scope of this study the characterisation of slip, as one of many flow instabilities, from rheological behaviour of chosen commodity material PE with various molecular structure, namely, linear HDPE, linear LLDPE with short branches and long branched LDPE, was selected as the suitable concept for evaluation of slip determination posibilities.

Rheology was characterized by the help of capillary rheometer Goetffert RG 50 allowing to carry out experiments in two different measuring modes, namely under controlled pressure or under controlled piston speed. Thus as the other goal of this work could be seen verification of posibility to employ commercial high-pressure capillary viscometer for evaluation of flow instabilities just as to define negative influence of used experimental modes. Such verification is useful way in order to show wheter description of complex rheological behaviour due to complicated expermintal evaluation (determination of acceptable experimental conditions for flow instabilities description) could be somehow simplified and consequently utilised as suitable tool for effectivity increase in new material developing stage and optimizing of processing conditions and tools [19].

3 EXPERIMENTAL CHARACTERIZATION

Rheological properties of three various polymer melts were determined by using high-pressure capillary viscometer in two different measuring modes at three different temperatures 150°C, 170°C and 190°C, chosen according to possible manufacturing conditions and as temperatures emphasizing slip tendency. Heating were achieved by the help of heated barrel which is part of used rheometer. In order to provide and easy survey of data and eliminate its mismatch, temperatures of 150 and 190°C were elected as enough demonstrative. Thus only results for them are shown in following figures.

3.1 Used materials

In this study polyethylene, as one of the mostly used polymeric material often used for example as packaging material (plastic bags, plastic films, several containers, etc.), was tested. Polyethylene belongs to group of thermoplastic polymers having characteristic long molecular chain including only hydrocarbons. There are and several types of polyethylenes with various structural constitutions (linearity, branching) and molecular weight characteristic (average molecular weight, width of its distribution) and consequent crystallinity.

Used materials were chosen on the same polyethylene base but with different tendency of onset of flow instability represented by wall slip. A linear high-density polyethylene (HDPE) with high slip tendency, a linear low-density polyethylene (LLDPE) with short side branches created via copolymerization and moderate slip tendency and finally, a long branched low-density polyethylene (LDPE) were studied during the steady capillary flow due to verification of wall slip. *Figure 18* illustrates schematic branching of examined materials.

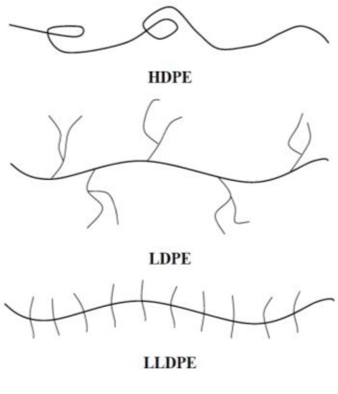
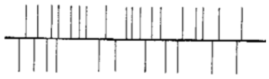
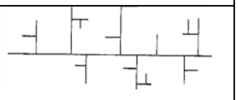


Figure 18: Schematic representation of the microstructure of HDPE, LDPE and LLDPE [16]

While almost no branching of a high-density polyethylene causing lower level of entanglement of their molecular chains increase tendency to slippage, high entanglements of LDPE molecules reduce it. Different sensitivity of slit to temperature and pressure conditions were described as well as to different viscosities, molecular weights and molecular structures [20].

Table2: Structure and properties of used materials.

	HDPE	**LLDPE**	**LDPE**
Labelling	Liten FB85F	Borealis Borstar FB2230	Bralen FB-2-17
Density [g/cm^3]	0,94 – 0,96	0,92 – 0,93	0,91 – 0,93
Tendency to slip	Strong	Half	Weak
Melt temperature [°C]	125	124	105
Scheme of branching			

It is known that there is different sensitive to temperature and pressure between used materials as well as different viscosities due to different molecular weights and molecular structures [20, 21].

3.2 Utilized equipment

In this work shear viscosities of polymer melts were measured by the help of capillary rheometer Goettfert RG 50, which is shown in *Figure 19.* It consists of two pistons with possibility of control their speed, which are inserted in two separated heated barrels ended with capillaries. While the whole barrel of rheometer is divided in three individual temperature regions for better temperature control, just one temperature was set in this case with allowed deviation value of 0,5°C for all over the barrel.

Two possible experimental measuring modes based on control pressure or control piston speed were applied in order to measure different flow behaviour influenced by flow instabilities in different way. Measured data are plotted in several figures demonstrating the selected dependencies of quantities which are required for determine of flow behaviour and its instabilities.

Figure 19: Photo of Goettfert RG 50

Material in form of granules was stuffed and melted in the pre-heated reservoir, where it was consequently pressed with pistons in order to avoid material degradation, which could be influenced by presence of oxygen. Set melting time of 5 minutes was chosen as long enough not only to achieve total temperature homogeneity but also to reach relaxed state of material.

Figure 20: Photo of used capillaries, namely with L/D ratio: 40/2; 20/1; 10/0.5 and orifice 0.1/1 mm

At the bottom of reservoir was fixed capillaries, which through the material goes onwards to capillary end where it exits out of the rheometer. Experiments were performed using a series of long (*L/D*: 40/2; 20/1 and 10/0.5 mm note that even the used capillaries had various diameter, the same *L/D* ratio was employed) and orifice (0.1/0.5; 0.1/1; 0.1/2) dies, which are shown in *Figure 20,* in order to determine entrance pressure, which is needed for entrance pressure determination necessary for Bagley correction.

3.3 Capillary rheometry measurements

Rheological measurements at various conditions (three temperatures, three capillaries set (long and orifice), and two measuring modes) were carried out on the tested materials.

As first few measurements in control piston speed mode (range of shear rates from 10-200 reciprocal seconds) was performed in order to characterize precursory region of measured pressures region. According to the measurements results, set of pressure values, namely 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130 and 140 bar, for control pressure mode, which were kept constant for each measured point was utilised for viscosity data evaluation. During this measurement, the pressures in the both reservoirs were separately scanned utilizing pressure transducers with appropriate measurable pressure range. The pressure difference, (Δp), was consequently calculated from subtraction of long (p_1) and orifice (p_2) capillary pressure values

$$(p_1 - p_2 = \Delta p) \tag{10}$$

Recorded shear rate was calculated from velocity of piston in every each step of measurement, consequently to the pressure value stabilization. In this way values of viscosity at various shear rates were determined according to set constant pressures. Applied pressure is controlled through the backward correction of piston speed, which is changed automatically by internal rheometer sftware in order to achieve pressure steady state. In other words, even the pressure is controlled in this measuring mode, piston speed is changed during searching of corresponding shear rate level. After its finding the actual experimental data of all measured and calculated quantities are recorded and shear rates are plotted as function of applied pressure for the purpose of Mooney plot construction.

Control piston speed mode is the second possibility how to measure and evaluate wall slip by Mooney plot. The same parameters are determined nevertheless other quantity (piston speed) is controlled at constant rate which is set by default at interval 1-2000 s^{-1}. All measurements were made at same constant shear rate values (1, 2, 3.5, 5, 7, 10, 20, 35, 50, 70, 100, 200, 350, 500, 700, 1000, 2000) s^{-1}.

Table 3: Experimental conditions used for HDPE, LLDPE and LDPE rheological behaviour determination

Temperatures [°C]		
150	170	190

Capillaries [L/D]		
10 / 0.5 0.1 / 0.5	20 / 1 0.1 / 1	40 / 2 0.1 / 2

Shear rate [s^{-1}]																
1	2	3,5	5	7	10	20	35	50	70	100	200	350	500	700	1000	2000

Pressure [bar]											
30	40	50	60	70	80	90	100	110	120	130	140

4 RESULTS AND DISSCUSION

Since the objective of this work was beside the study of wall slip flow instabilities implementation performed based on capillary rheological measurements also evaluation of suitability to utilised high-pressure capillary rheometer Goettfer Reograph 50 for Mooney correction determination, two various available experimental modes were applied for flow behaviour description. Determined Mooney plots constructed from dependencies of shear rates as a function of pressure determined directly at chosen shear stress conditions using selected capillaries (pressure control mode) was compared to Mooney plots constructed from the same dependencies however chosen shear stress conditions were determined via mathematical data interpolation recorded in shear rate control mode, as it will be closely described further.

4.1.1.1 Control pressure mode

Presented *Figures 21* and *22*, which contain measured flow data for HDPE, LDPE and LLDPE at temperatures of 150 and 190°C evaluated with capillaries with various L/D ratios, are composed by directly recorded shear rate values calculated from piston speed as a function of set pressure values determining shear stress. It could be noted that shear rate increases as the pressure arises for each of used materials and capillaries. Even data recorded using capillaries with bigger diameters (1 and 2 mm) seem to be stable, observed errors during data measurements with small diameter capillaryy (0,5 mm) indicate colossal data variations, as it clear from the presented graphical results. There is assumed the most expressive manifestation of the wall slip whereas no slip occurs with infinitely large diameter. Smaller deviations are obvious during measurements at higher temperatures what could be explained other by the decrease of critical stress or by an introduction of critical temperature where the slip do no occurred. It should be highlighted that observed data spread significantly excess the slip theory which cause the impossibility to further evaluate measured data.

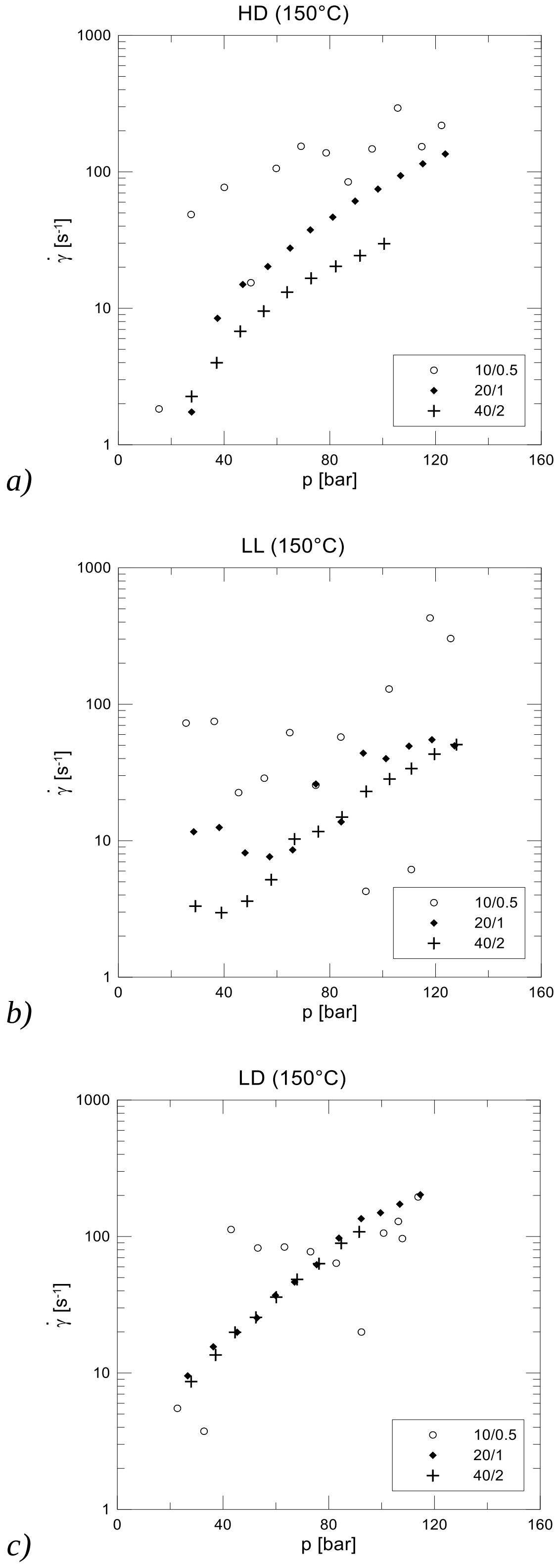


Figure 21: Shear rate as a function of pressure conditions determined during flow measurements under control pressure mode with capillaries of L/D ratios 10/0,5. 20/1 and 40/2 at temperauture of 150°C for a) HDPE, b) LLDPE, c) LDPE

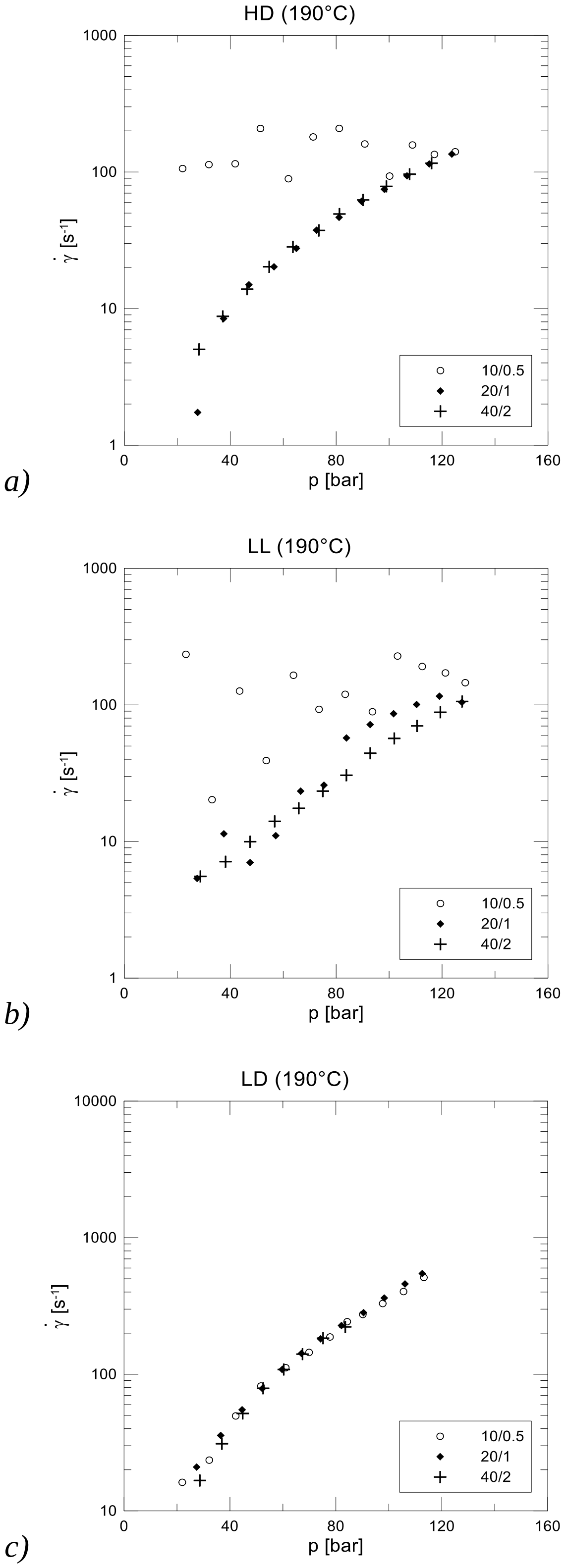


Figure 22: Shear rate as a function of pressure conditions determined during flow measurements under control pressure mode with capillaries of L/D ratios 10/0,5; 20/1 and 40/2 at temperauture of 190°C for a) HDPE, b) LLDPE, c) LDPE

Based on results presented in *Figure 23-25*, it could be stated that as the main cause of error was detected the stabilization of pressure level. For introduction of this problem the time establishing of the pressure level of 30 bar during the piston velocity approximation, automatically performed by internal software of capillary rheometer, for all tested materials at the same temperature 150°C was chosen and presented. Obviously, shear rate values were flickering in the wide range when the demanded pressure value was approximated. For easier comparison of tested materials the changing values of shear rate are displayed in the same scale for each capillary diameter employed. As it is clear from the graphical results comparison, pressure value is stable only in the case of utilisation of the capillary with the biggest diameter (2 mm). On the other hand in the case of smaller diameters significant variations of shear rate determined by piston velocity were obviously observed, moreover these variations were not disappearing thus leading to absolutely not steady value of shear rate even after long time of measurement. In other words that means that it is absolutely not possible to evaluate Mooney correction. In connection with this finding, it could be stated that, since it depends just on the moment when the shear rate value is recorded by rheometer, it is impossible to obtain unique value of shear rate, hence data presented in *Figure 21* and *22* are disordered. Due to this fact a reason of a giant disorder in control pressure mode was studied and other way of slip evaluation were proposed. Control piston speed mode was thus employed as the second possible substitution for Mooney plot evaluation.

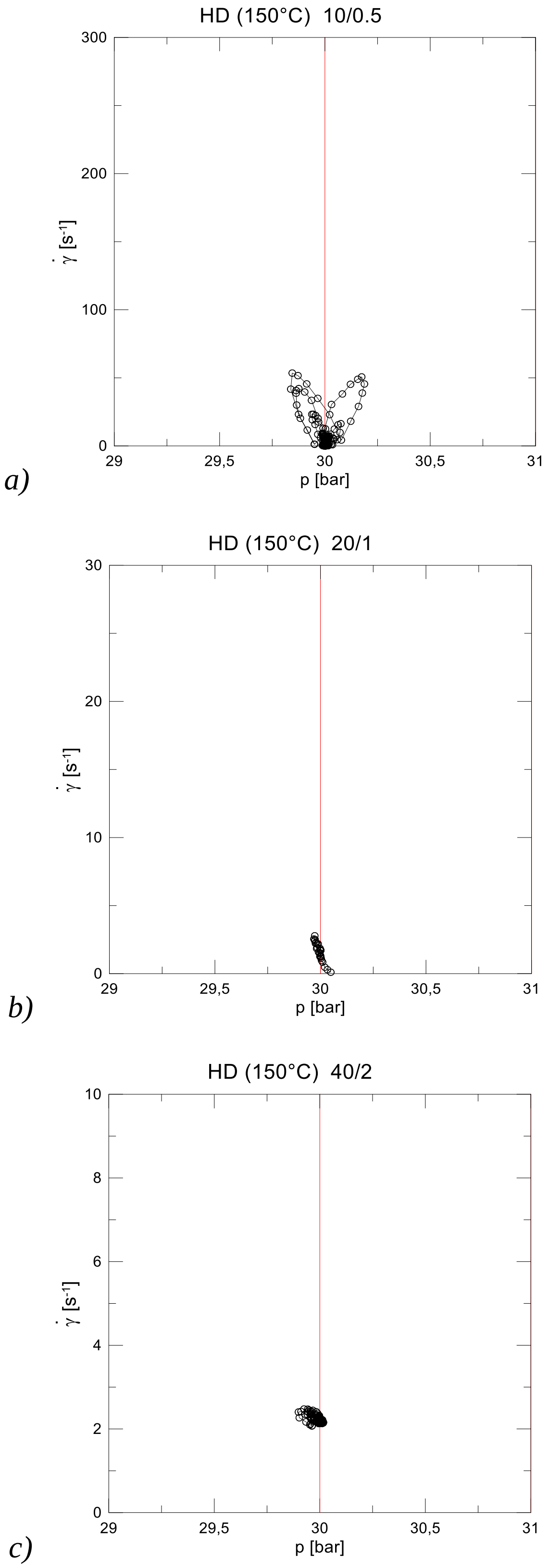


Figure 23: Shear rate stabilization at temperature of 150°C for HDPE at pressure 30 bar defined for L/D ratios a) 10/0.5; b) 20/1; c) 40/2

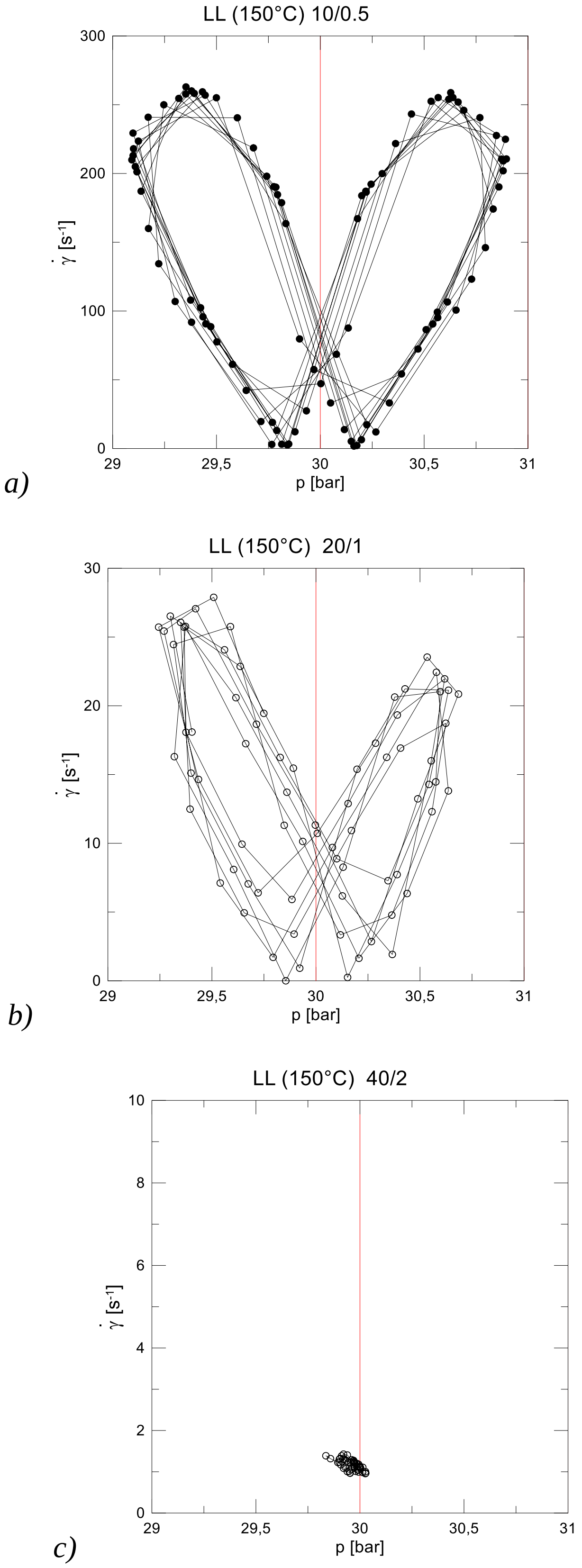


Figure 24: Shear rate stabilization at temperature of 150°C for LLDPE at pressure 30 bar defined for L/D ratios a) 10/0.5; b) 20/1; c) 40/2

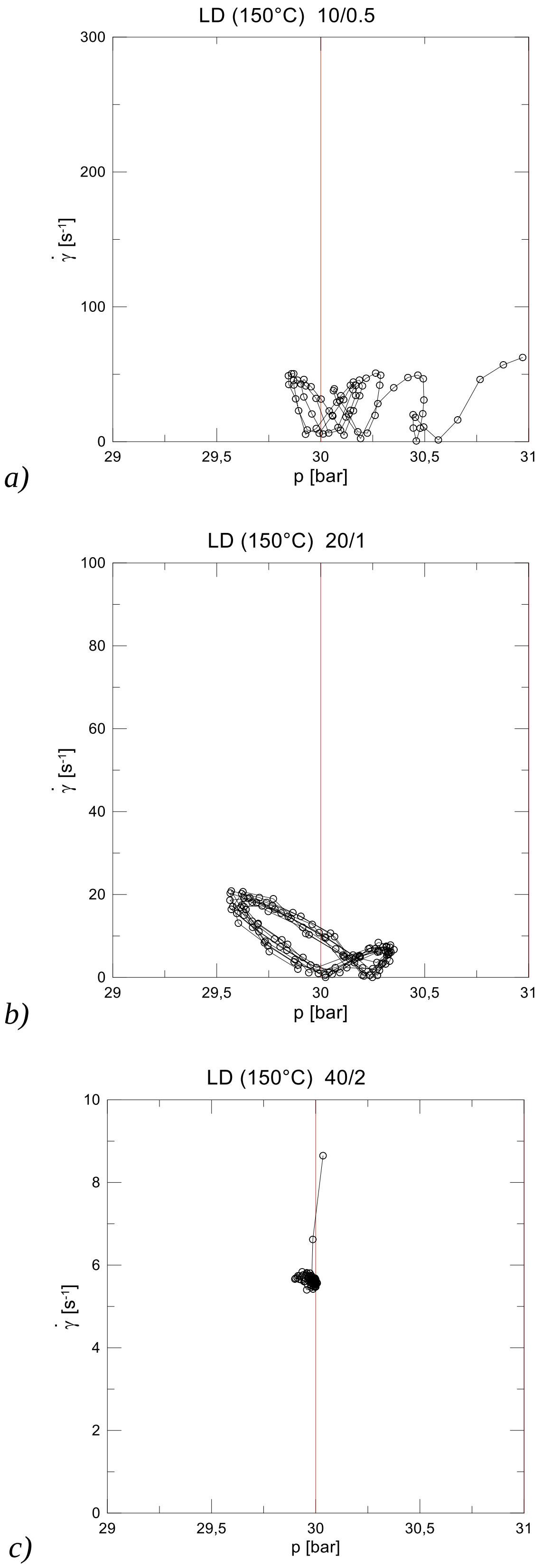
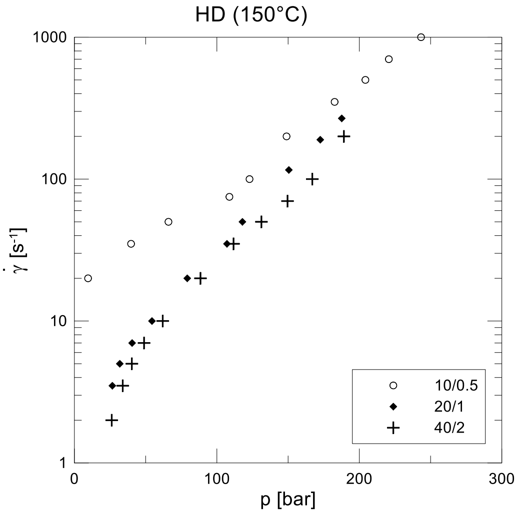


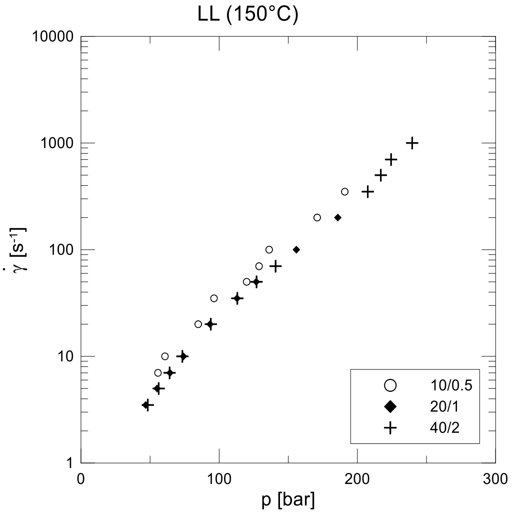
Figure 25: Shear rate stabilization at temperature of 150°C for LDPE at pressure 30 bar defined for L/D ratios a) 10/0.5; b) 20/1; c) 40/2Control shear rate mode

Since the shear rate-pressure data determined in controlled pressure mode was found to be highly inaccurate, determination of wall slip using controlled shear rate mode of capillary rheometer was checked as another attainable evaluation approach. In this case the constant values of pressure (shear stress) was determined only via mathematical interpolation of the shear rate-pressure behaviour presented in Figure 22. For determination of shear rates at defined constant pressure values (the same levels as used for data evaluation in controlled pressure mode) measured data was interpolated via power function.

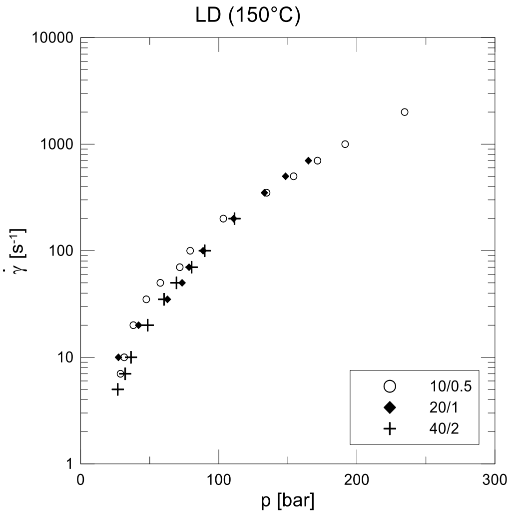
Comparing results displayed in *Figure 26* it is obvious that the branching of polymer melts has considerable influence at onset of the wall slip, indicated by the spread of curves determined for each capillary L/D ratio. Namely, while the most settled data thus almost unique behaviour of shear rate-pressure dependencies were recorded with employed capillaries for branched low-density polyethylene (see *Fig. 26c*), indicating no disposition for slippage, linear structure of high-density polyethylene evoked strong slippage tendency (*Fig. 26a*), particularly for the smallest diameter 0,5mm. In the case of linear low density polyethylene (*Fig. 26b*) the moderate tendencies to flow instabilities origin were determined.



a)



b)



c)

Figure 26: Shear rate as a function of pressure conditions determined during flow measurements under control shear rate mode with capillaries of L/D ratios 10/0,5; 20/1 and 40/2 at temperauture of 150°C for a) HDPE, b) LLDPE, c) LDPE

4.2 Wall slip characterization

As it was described above, dependencies of shear rate-pressure data evaluated via interpolation at selected pressure values could be employed for construction of Mooney plots. Examples of Mooney plots consisting of shear rates as a function of radius reciprocal values for all tested materials at temperature of 150°C and chosen pressure conditions are presented in *Figure 27*. Slip velocity could be evaluated from presented results and discussed directly in connection with the curve slopes of data at constant pressure values. As it is obvious from comparison of graphical results displayed in the *Figure 27*, while the slip velocity of HDPE was found to be significant, it was moderate and zero for LLDPE and LDPE, respectively.

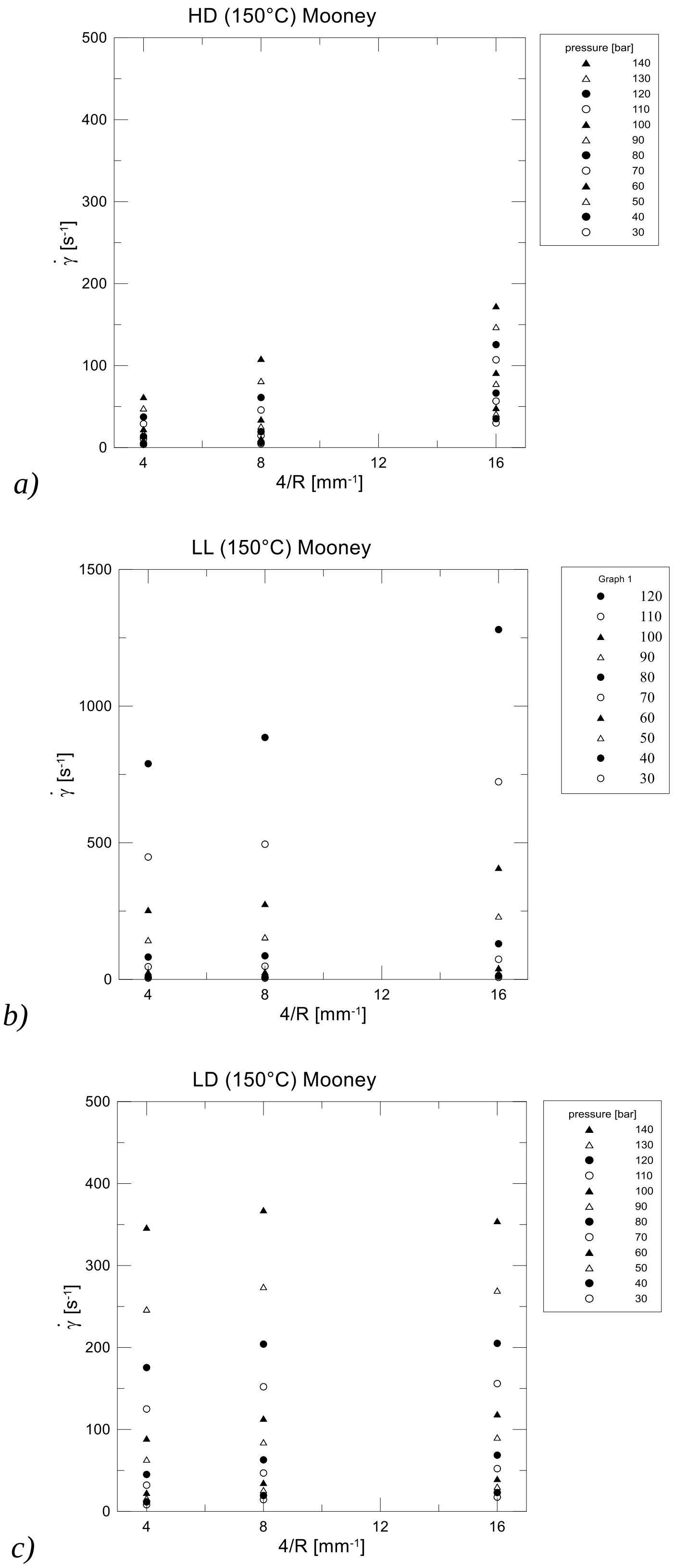


Figure 27: Mooney plot at various pressure conditions at temperature of 150°C evaluated for a) HDPE, b) LLDPE, c) LDPE

CONCLUSION

Viscosity of polymer materials is thought as an important and fundamental property usable for example for description of its flow behaviour during polymer melt processing. Since the viscosity evaluation could be vitally affected by flow instabilities as wall slip, which could cause inaccuracies in processing modelling, possibility to describe these instabilities is crucial for further appropriate viscosity utilisation. It could be stated, based on the performed study, that despite the offered advantage of direct evaluation of Mooney correction via controlled pressure experiments, the standard setting of capillary viscometer Rheograph 50 is not suitable for direct evaluation of the polymer melt slip on the capillary wall. Utilisation of experimental controlled shear rate viscosity data interpolation via mathematical procedure was revealed as much more advantageous for the wall slip determination.

REFERENCES

[1] VLACHOPOULOS, J. *Polymer Rheology and Processing.* Intensive Short Course. Ontario, Canada: McMaster University [1994].

[2] SHAW, Montgomery T. *Introduction to polymer rheology*. Hoboken, New Jersey: Wiley, [2012], xiv, 395 pages. ISBN 978-047-0388-440.

[3] SEDLACEK, Tomas. *Pressure dependence of polymer melts rheological properties*. Zlin: Tomas Bata University, 2004. ISBN 80-731-8240-8.

[4] AHO, Johanna. *Rheological Characterization of Polymer Melts in Shear and Extension: Measurement Reliability and \data for Practical Processing* [online]. [cit. 2015-02-10]. Available from: http://URN.fi/URN:NBN:fi:tty-2011050914663

[5] MACOSKO, Christopher W. *Rheology: principles, measurements, and applications*. 11. print. New York: Wiley-VCH, 1994. ISBN 978-047-1185-758.

[6] *Tokové chování polymerních tavenin – reologické modely* [online]. [cit. 2015-03-08]. Available from: z: http://ufmi.ft.utb.cz/texty/fyzika_pol/FP_02.pdf

[7] MUSIL, Jan. *Development of Improved Entrance Pressure Drop Technique for Extensional Viscosity Determination*. Zlin: Tomas Bata University, 2008. Master Thesis.

[8] ZWEIFEL, Hans a St AMOS. *Plastics additives handbook*. 5th ed. Cincinnati, OH: Hanser Gardner Publications, 2001, xxxvi, 1148 p. ISBN 15-699-0295-X

[9] SEDLACEK, Tomas. *The Role of Pressure in the Flow Behaviour of Polymeric systems: Application and Implementation.* Zlin: Tomas Bata University, 2013. Habilitation Thesis.

[10] LAUN, Hans Martin. Capillary rheometry for polymer melts revisited. *Rheologica Acta*. 2004, 43(5): 509-528. DOI: 10.1007/s00397-004-0387-2.

[11] JAN MEWIS, Norman J. *Colloidal suspension rheology*. Cambridge: Cambridge University Press, 2012. ISBN 978-113-9154-383.

[12] SMILLO, Fabricio. *Wall slip and spurt of molten polymer*. Ottawa: Library and Archives Canada = Bibliothèque et Archives Canada, 2006. ISBN 04-940-6587-7. Master Thesis.

[13] DELGADILLO-VELÁZQUEZ, O., G. GEORGIOU, M. SENTMANAT a S.G. HATZIKIRIAKOS. *Sharkskin and oscillating melt fracture: Why in slit and capillary dies and not in annular dies?* ISBN 10.1002/pen.20939

[14] DENN, Morton M. E XTRUSION I NSTABILITIES AND W ALL S LIP. *Annual Review of Fluid Mechanics*. 2001, **33**(1): 265-287. DOI: 10.1146/annurev.fluid.33.1.265. ISSN 0066-4189. Avaliable from: http://www.annualreviews.org/doi/abs/10.1146/ annurev.fluid.33.1.265

[15] HATZIKIRIAKOS, S. G. Wall slip of molten high density polyethylene. I. Sliding plate rheometer studies. *Journal of Rheology*. 1991, **35**(4). DOI: 10.1122/1.550178.

[16] ANSARI, Mahmoud, Yong W. INN, Ashish M. SUKHADIA, Paul J. DESLAURIERS a Savvas G. HATZIKIRIAKOS. *Wall slip of HDPEs: Molecular weight and molecular weight distribution effects*. ISBN 10.1122/1.4801758.

[17] HATZIKIRIAKOS, Savvas Georgios a Kalman B MIGLER. *Polymer processing instabilities: control and understanding*. New York: Marcel Dekker, 2005, x, 470 p. ISBN 08-247-5386-0.

[18] MUSIL, J., ZATLOUKAL, M., GOUGH, T., MARTYN, M. Experimental Investigation of Die Drool and Slip-stick Phenomena during HDPE Polymer Melt Extrusion. AIP Conference Proceedings 2011, vol. 1375, pp. 26-42, ISSN 0094-243X. Avaliable from: http://www.wseas.us/e library/conferences/2012/CambridgeUSA/FLUHMABE/FLUHMABE-24.pdf

[19] DOMBROWSKI .., Walter Michaeli. With contributions by Ulrich.. *Extrusion dies for plastics and rubber: design and engineering computations*. 3., rev. ed. München [u.a.]: Hanser, 2003. ISBN 978-344-6225-619

[20] ANSARI, Mahmoud, Savvas G. HATZIKIRIAKOS a Evan MITSOULIS. Slip effects in HDPE flows. *Journal of Non-Newtonian Fluid Mechanics*. 2011. DOI: 10.1016/j.jnnfm.2011.09.007.

[21] KALYON, Dilhan M. a Halil GEVGILILI. Wall slip and extrudate distortion of three polymer melts. *Journal of Rheology*. 2003, **47**(3): 683-. DOI: 10.1122/1.1562156. ISSN 01486055.

ABREVIATION

PE	*polyethylene*
HDPE	*high-density polyethylene*
LDPE	*low-density polyethylene*
LLDPE	*linear low-density polyethylene*
RG	*rheograph*
UV	*ultra violet*

SYMBOLS

A	*surface area*
D	*capillary diameter*
dx	*length derivation*
E	*Young´s modulus for tension*
F	*force*
G	*shear modulus*
h	*distance*
L	*die length*
n	viscosity shear thinning exponent,
p	*pressure*
Δp	*pressure difference*
Δp_e	*entrance pressure drop*
Q	*volumetric flow*
R	*die radius*
v	*speed*

$\dot{\gamma}$	*shear rate*
$\dot{\gamma}_A$	*apparent shear rate*
$\dot{\varepsilon}$	*extensional rate*
η	*shear viscosity*
η_e	*elongational viscosity*
τ	*shear stress*
$\dot{\tau}_A$	*apparent shear stress*
τ_e	*elastic shear stress*
τ_w	*wall shear stress*

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