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Applied rheology for polymers: From characterization to modeling and flow instabilities

Aplikovaná reologie pro polymery: Od charakterizace k modelování a tokovým nestabilitám

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Macromolecular Chemistry

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ABSTRACT

In this summary of a Thesis, our work on applied rheology for polymers is introduced and the most important findings are emphasized. In the first chapter, *Introduction*, overview of the studied research subject is provided. The second chapter *Novel experimental methodologies for rheological characterization of polymer melts* summarizes our findings in area of experimental rheology of different polymer melts (HDPE, LDPE, LLDPE, PP, PC, PMMA, and PS). Introduction of innovative method of determining the uniaxial extensional viscosity from the entrance pressure drop of orifice dies and assessment the role of the pressure on the melt rheology can be considered as the most important results in this area. The third chapter *Development and evaluation of new constitutive equations for polymer melts* presents research in area of the physics of polymer motion with respect to macroscopic flow phenomena. The most valuable contribution here is development of advanced constitutive equations discriminating between different topologies of polymers, which are suitable for realistic polymer processing simulations. The fourth chapter *Theoretical and experimental investigation of flow instabilities occurring during polymer processing* provides a fundamental research on understanding of unwanted flow phenomena occurring during flow and processing of polymer melts. Key contributions to this research field are, first, development of advanced viscoelastic finite element modeling and novel criteria allowing prediction of interfacial instability onset in coextrusion. Second, development of variational and minimum energy principles based model allowing modeling of free surface flow instabilities in film blowing. Finally, discovery of factors (negative pressure at the die exit and flow induced molecular weight fractionation) allowing to explain die drool phenomenon occurring during the extrusion. The fifth chapter *Applied rheology for production and characterization of polymeric nanofiber based filters* introduces novel rheology based methodologies allowing to optimize production of polymeric nanofibers as well as to characterize nanofiber based filters. The most valuable contribution here is development of the 3D model allowing to model slip around the polymeric nanofibers considering ‘non-Newtonian’ character of the filtered media.

CONTENTS

1 Introduction

Applied rheology for polymers represents research area having interdisciplinary character combining polymer science, mechanics, chemical/mechanical engineering, thermodynamics and mathematics [1-19]. In the first part of this Thesis, the main attention is paid to the polymer melt rheology and its role in polymer processing. Due to the fact that polymer melts behaves as non-Newtonian viscoelastic fluids, their flow behavior is rather complex and leads to number of flow phenomena which have negative impact on their processing and final product properties [15-19]. The polymer melt elasticity, high shear viscosity, extensional viscosity and its tendency to slip at the solid surfaces causes the flow destabilization. This is in contrast to Newtonian fluids for which the inertial forces and surface tension are usually main important parameters [15]. For polymer melts, the typical flow instabilities are following: melt fracture (surface melt fracture - sharkskin, cyclic melt fracture, gross melt fracture) and die drool phenomenon (unwanted accumulation of the material at the die exit) in extrusion; draw resonance (spontaneous variation in basic dimensions of the extrudate during its stretching) and necking in fiber spinning, film casting and film blowing; the encapsulation (tendency of one fluid to encapsulate another fluid during the flow) and interfacial instabilities (distortion of the interface between two coextruded polymer melts) in coextrusion. In order to understand the flow instabilities, the research must be performed in these areas as shown in the first part of this Thesis:

- Investigation the relationship between the molecular structure of molten polymers and their rheological behavior in different flow situations as well as development and testing of novel constitutive equations, which allow predicting stress responses of polymer melts in wide range of flow situations realistically. However, this is difficult, firstly, due to their broad molecular weight distribution, complex chain and branching structures involving multidimensional distributions that can be neither be predicted nor characterized with precision [9] and secondly, due to experimental difficulties connected with the correct and precise determination of basic rheological characteristics, especially in the extensional flows [6, 8, 10-11].
- Detailed experimental investigation of flow instabilities occurring during polymer processing for different polymers, equipment designs and processing conditions followed by modeling of polymer processing utilizing proper numerical technique to solve mass, momentum and energy balance equations together with chosen constitutive equation.

- Development of theories and suitable criteria to understand, plausibly explain and even predict the relationship between molecular structure of polymer melts, rheological behavior, equipment design, processing conditions and process stability.

In the second part of this Thesis, the attention is paid to the utilization of basic rheological tools for optimization of polymeric nanofibers production for gas filtration purposes as well as for their characterization.

2 Novel experimental methodologies for rheological characterization of polymer melts

Precise evaluation of basic rheological characteristics of molten polymers in shear and especially in elongational flows, at which macromolecules are the most strongly aligned, is highly important for better understanding of their molecular structure and processing [1-19]. However, due to the fact that generation and control of the polymer melt flows (primarily extensional ones) at wide range of temperatures/pressures and deformation rates is difficult, experimental determination of their rheological characteristics might be highly challenging task [6, 8, 10-11]. The works reported in this section focus on this research subject and provides important findings, suggestions and even introduces new methodology proposals and their evaluation.

A simple method has been developed for the estimation of the linear viscoelastic relaxation spectrum from capillary viscosity data [A1]. For that purpose, a modified Leonov model was employed and the relaxation spectra and model parameters were estimated through nonlinear regression using measured steady shear viscosity data and uniaxial extensional viscosity data calculated from Cogswell's method. Using the proposed methodology, the relaxation spectra of several resins (LDPE, LLDPE, PP and PS) were estimated and they were used in a Maxwell model to predict the linear viscoelastic properties of these resins. The predicted properties (storage and loss moduli and complex viscosity) were found to be in very good agreement with data from oscillatory shear measurements, thus supporting the validity of the estimated relaxation spectra and proposed technique.

Two different methodologies for determination of polymer melt tensile strength properties were utilized and evaluated for two LDPEs and two metallocene LLDPE resins through capillary rheometry and Haul-off (Rheotens-like) measurements [A2]. It has been shown that, firstly, polymer melt tensile strength characteristics determined by both methods are comparable only if there is no slip at the capillary die and

secondly, these values can be correlated to the drawability in tubular film blowing for corresponding materials.

Specific type of back-pressure device for capillary rheometer together with temperature/pressure dependent modified White-Metzner model were used to evaluate the effect of pressure and temperature on the shear and uniaxial extensional viscosities of different polymer melts (HDPE, LDPE, LLDPE, PP, PC, PMMA, and PS) and simple relationships between pressure and temperature sensitivity coefficients were obtained for individual polymers [A3].

Viscoelastic 2D finite element simulation utilizing modified White-Metzner constitutive equation followed by corresponding experimental work were used to improve methodology for steady uniaxial extensional viscosity determination of polymer melts from entrance flows taking the place in capillary rheometers [A4-A5]. Key obtained results are introduction of novel rheological parameter ‘entrance viscosity’, new methodology called ‘effective entry length correction’ and novel die design (which was patented recently [P1]) - all improving the capability of the Cogswell, Binding, and Gibson models to estimate the steady uniaxial elongational viscosity from entrance pressure drop measurements. The proposed methodology and novel die design were successfully tested for different types of polymers such as metallocene LLDPEs, LDPEs and HDPE.

3 Development and evaluation of new constitutive equations for polymer melts

The constitutive equation can be viewed as the mathematical representation of the polymer melt flow behavior allowing to predict the stress response for given flow situation. Having suitable set of basic rheological characteristics determined experimentally, all model parameters can be identified and consequently used for polymer structure assessment. The key requirement for constitutive equations is their capability to describe the flow behavior of polymer melts at different flow situations realistically. Modeling of polymer processing by using proper constitutive equation can then be used for optimizing equipment design and processing conditions. Bellow, contribution to this research subject is described.

Advanced constitutive equation, modified Leonov model, which is based on irreversible thermodynamics, molecular theories discriminating between different topologies of polymers and is suitable for realistic polymer processing simulations was proposed in [A6]. The

fitting/predicting capabilities of the proposed modified Leonov model were consequently compared with molecular based eXtended Pom–Pom models in shear and uniaxial extensional flows for LDPE, mLLDPE, PVB [A6], two LDPEs having different level in chain branching [A7], and two virtually linear polymer melts (metallocene LLDPE, HDPE) [A8] and very good agreement between the measured data and modified Leonov model fittings/predictions was found. Due to its high capability to represent flow behavior of polymer melts realistically, the developed model was successfully utilized in the finite element based simulations for understanding of interfacial instabilities occurring during coextrusion of polymer melts as shown in [A9-A14]. The utilization of molecular based constitutive equations to assess structure of molten polymers from measured rheology data was tested in [A15] for different metallocene PPs. It was found that long chain branching level for tested samples can be quantified from the utilized XPP model parameters i.e. through the dependence of number of arms (branches) vs. orientation relaxation time (which is proportional to the length of the chain).

Finally, a simple phenomenological generalized Newtonian law model was developed and tested by using rheological data taken from the open literature for different polymer melts [A16]. In this model, viscosity is given as a specific function of three principal invariants of the deformation rate tensor, *D*, and its absolute value defined as square root of D*D. It has been found that the model predictions are in very good agreement with the strain rate dependent steady shear and uniaxial extensional viscosities for linear and branched polyolefines. The model behaves correctly in description of steady planar and equibiaxial extensional viscosities and allows their independent strain hardening level control with respect to uniaxial extensional viscosity. The proposed model has already been successfully used in the modeling of polymer processing to understand film blowing instabilities as shown in [A17-A19].

4 Theoretical and experimental investigation of free surface flow instabilities occurring during polymer processing

In this section, basic types of free surface flow instabilities are introduced and our contributions to this research area are provided.

4.1 Interfacial instabilities

The coextrusion process can be used to produce multi-layer sheet, blown film, cast film, tubing, wire coating, profile and others. It has been used since the early 1950's to improve product quality and process efficiency. However, under certain conditions, the flow of viscoelastic polymeric materials gives rise to unstable interfaces and undesirable layer distribution, which can significantly affect the product properties (see Figure 1). In the open literature [20-42, A9-A14], two main types of interfacial instabilities have been detected; zig-zag (high frequency, low amplitude) – and wave (high amplitude, low frequency) and both types of interfacial instabilities can occur simultaneously on the film, as visible in Figure 2.

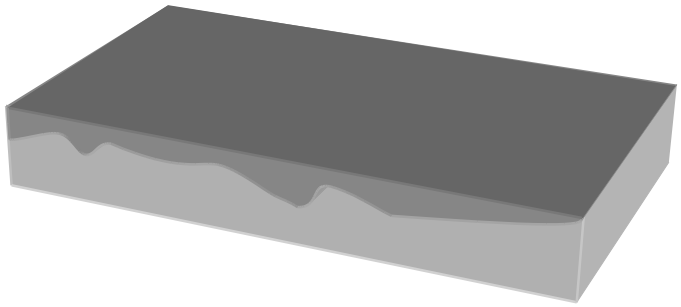

Figure 1. Sketch of the Interfacial instabilities in coextrusion [A9]. © John Wiley and Sons. Reproduced by permission of JohnWiley and Sons. Permission to reuse must be obtained from the rightsholder.

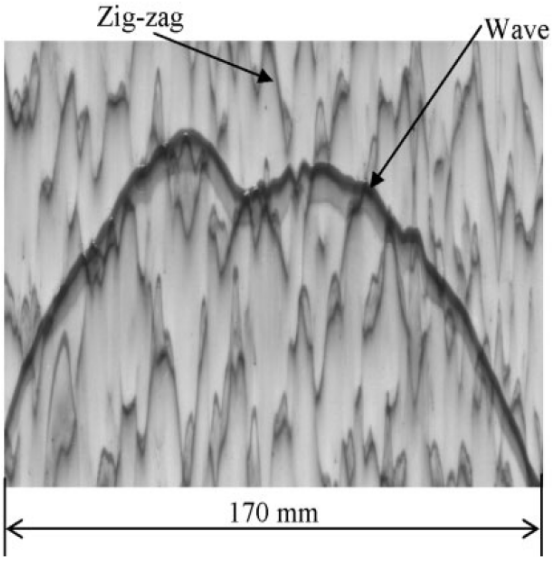

Figure 2. A photograph of a film sample exhibiting simultaneously wave and zig-zag type of interfacial instabilities [A9, A10]. © John Wiley and Sons. Reproduced by permission of JohnWiley and Sons. Permission to reuse must be obtained from the rightsholder.

Zig-zag instabilities have been shown to be connected with the end of the die, where the shear stresses usually achieve high values [21-25]. This type of instability can be captured via critical shear stress or recoverable shear on the interface [24-25]. Detailed experimental and theoretical study has been recently performed to determine the critical interfacial shear stresses for variety of LDPEs with different MWD [31]. It has been found that the critical shear stress on the interface may vary significantly i.e materials with broad MWD were found to be more sensitive to the zig-zag instability compare to LDPEs with a narrow MWD.

On the other hand, wave instabilities seem to be linked with the merging area in which intensive layer stretching occurs [20-23, 27-29, 36, 37, 38-40, 41-43, A9-A14]. To understand these instabilities, TNSD sign criterion, which quantifies the relative stretching of the coextrusion layers in the merging area, or extensional viscosity is usually used [20, 26, A11-A12, 27, A9, 36, 37, A14].

4.1.1 Merging area, wave type of interfacial instabilities and TNSD sign stability criterion

In practice, the stability of the coextrusion interface is usually evaluated through the local interface stress state according to Schrenk et al. [24], and Mavridis and Shroff [25]. They concluded that minimizing the interfacial shear stress and matching the elastic properties of the adjacent layers at the interface is an appropriate criterion for suppressing interfacial instabilities. However, Han and Shety [26] showed that although the critical shear stress theory is valid for a particular system, the critical shear stress value is affected by various factors, such as arrangement and thickness of the layers. Thus, it seems that the conditions for the occurrence of interfacial instabilities are more complicated than only the limitation on the interface shear stress. Recent experimental [20-23, 36, 39, A9], visualization [36, 37, 41-43, A14] and theoretical studies [27, 36, 38, 39, A9, A11-A12] suggest that the interfacial instability onset in the merging area is caused by intensive layer stretching. It has been observed experimentally [21-23, 36-37, A9, A14] that if the minor flow decreases, the stable coextrusion flow becomes unstable. To understand this behavior, a FEM simulation of such a flow field has been performed [A11] and some typical simulation results of this work are depicted in Figure 3a. Here, lines 1, 2 and 3 represent the interface shapes for the corresponding minor mass flow rates $\dot{m}_1$, $\dot{m}_2$ and $\dot{m}_3$; $\dot{m}_1 > \dot{m}_2 > \dot{m}_3$. It is visible that the interface gets closer to the wall for the decreasing flow rate in the minor layer, which

becomes intensively stretched. Such a flow situation is similar to capillary flow at which polymer melt is most stretched along the centerline at the entrance (see Figure 3b). In the coextrusion case, the maximum stretching does not need to be in the centerline because the minor flow is bounded by the moving interface and the die wall, contrary to capillary flow, where the flow is bounded by two walls. In other words, the maximum stretching does not occur on the interface but somewhere in the middle of the minor layer, as shown in Figure 4 [A11].

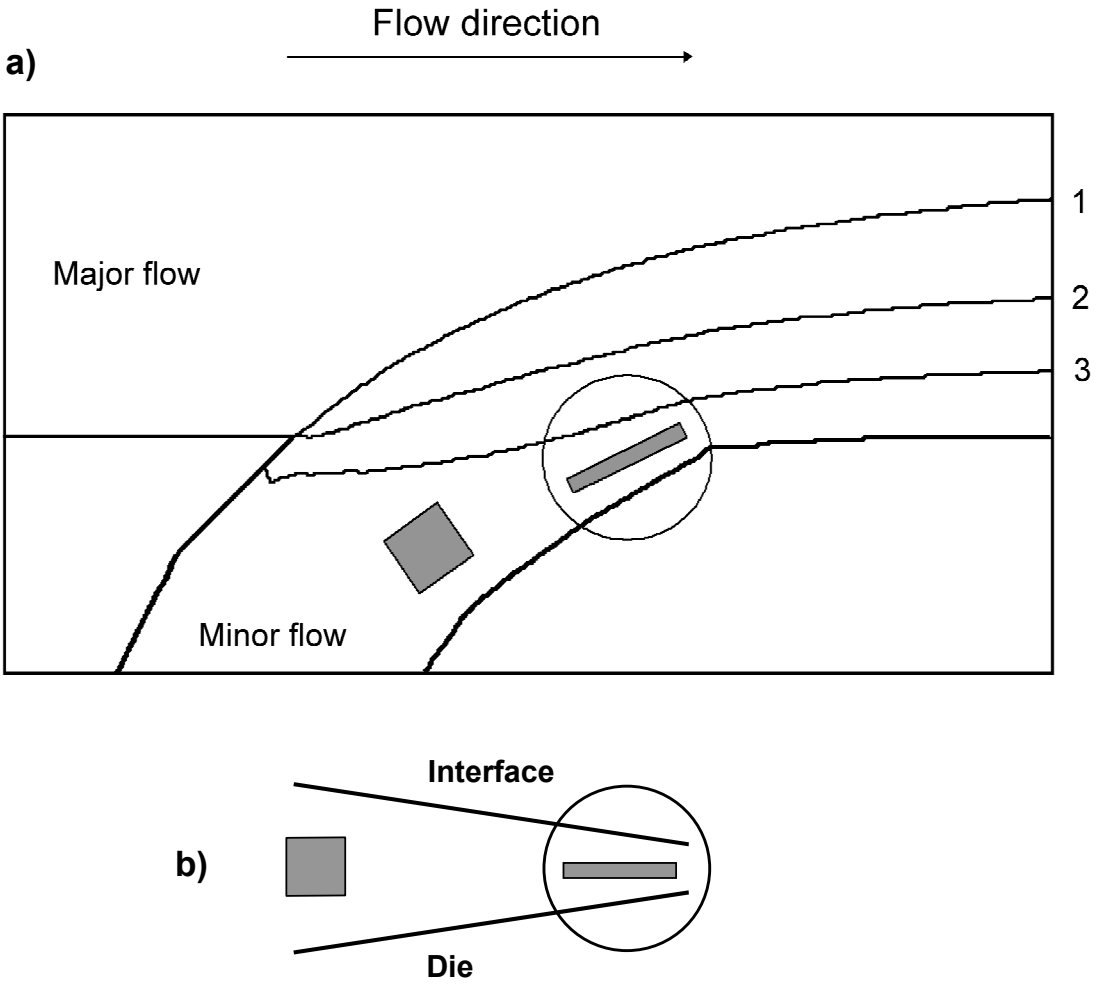

Figure 3. Visualization of merging area during coextrusion. **3a)** Typical shapes of predicted interfaces for decreasing mass flow rate in the merging point in the annular coextrusion die [A11]. **3b)** Detailed sketch of material element stretching in the merging area (capillary flow analogy) [A11]. © John Wiley and Sons. Reproduced by permission of JohnWiley and Sons. Permission to reuse must be obtained from the rightsholder.

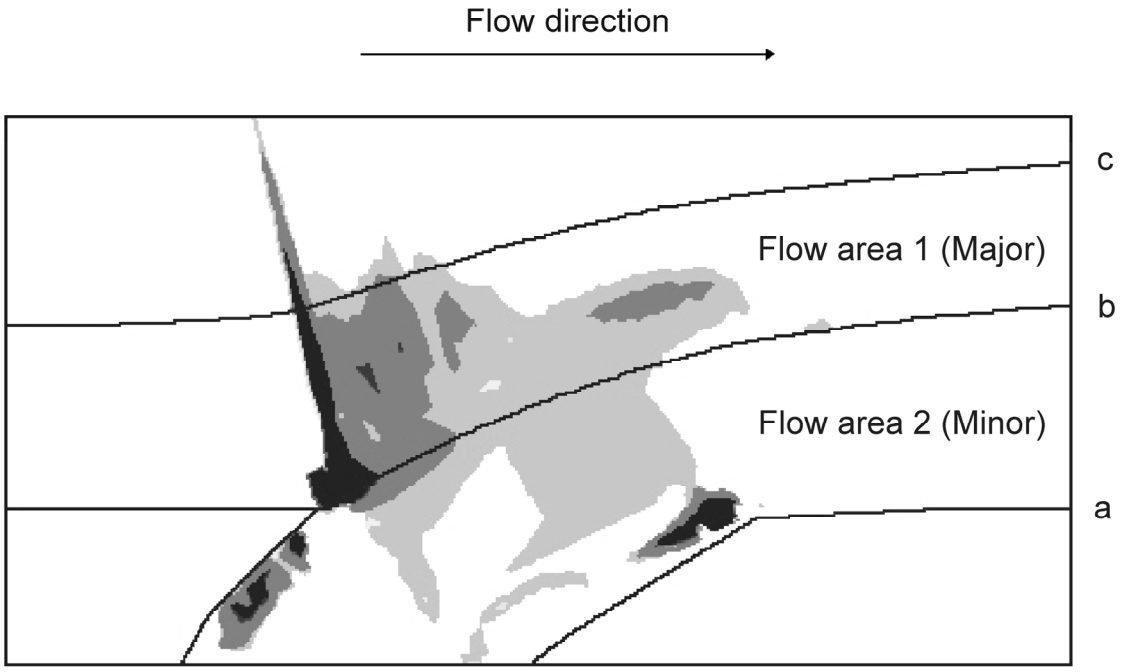

Figure 4. A typical shape of the predicted extensional rate field in the merge point during the flow in the annular coextrusion die [A11]. Here, a is the die wall; b-interface, and c-streamline. © John Wiley and Sons. Reproduced by permission of JohnWiley and Sons. Permission to reuse must be obtained from the rightsholder.

In this figure, the extensional rate field is shown in terms of dark regions (the darker the area, the higher the values of extensional rate). It is nicely visible that intensive stretching does not occur only at the interface (at its beginning) but also within the thickness of the layers. Thus, it seems that the way to understand interfacial instabilities can be through quantification of relative stretching of the coextruded layers across the interface in the merging area. To enable such quantification, the total normal stress difference (*TNSD*) value has been defined [A12]:

$$TNSD = \overline{N_{1,1}} - \overline{N_{1,2}} \qquad (1)$$

where $\overline{N_{1,1}}$ and $\overline{N_{1,2}}$ are average normal stress differences computed as the mean value in flow area 1 (major layer) and 2 (minor layer), respectively, over all streamlines in this areas (see Figure 4).

$$\overline{N_{1,1}} = \frac{1}{c-b}\int_{b}^{c} N_{1,1}(n)dn \tag{2}$$

$$\overline{N_{1,2}} = \frac{1}{b-a}\int_{a}^{b} N_{1,2}(n)dn \tag{3}$$

Flow area 1 is determined by the mass flow rate, which is the same as in flow area 2. Since in the merging area, mixed shear and extensional flow occurs, *TNSD* is generated by both the extensional and the shear flow components and can be found through a numerical simulation.

The reason for introduction of the *TNSD* is following: the amount of the first normal stress difference determines how particles in the flow area are stretched. Therefore, the *TNSD* is positive when the particles in the major layer are stretched more than the particles in the minor layer. The appearance of the negative sign, on the other hand, means that at this moment the minor layer is stretched more. When the *TNSD* value was calculated for two layer coextrusion that goes from stable to wavy unstable flow conditions (the minor flow decreased from 22% to 10% of the total mass flow rate), it was revealed that for the stable state *TNSD* is positive, while for the unstable state *TNSD* changes the sign or becomes negative within a particular relative position [A12] (0-1 represents the merging area) as depicted in Figure 5.

The physical meaning of *TNSD* is visualized in Figure 6. If *TNSD* changes the sign from positive to negative, the coextrusion interface moves towards the die wall due to the minor layer stretching, and subsequently it moves from the die wall due to the major layer stretching. This elastic after-effect evidently destabilizes the coextrusion flow. In an extreme case (when *TNSD* becomes strongly negative), the minor layer is stretched so much that it becomes very thin (the interface moves very close to the wall) and the layer breaks up. Of course, the question is why a small region of negative *TNSD* along the interface, relatively close to the merging point, should lead to instabilities and why it does not diminish. The explanation, provided in [A12] was following: the wave is created due to the elastic after-effect (Figure 7a) and the velocity rearrangement in the merge area may cause intensive wave stretching, as depicted in Figures 7b and 7c. It is believed [A12] that the irreversible nature of such drastic elongational deformations occurring just at the merge point of the layers may explain why wave instabilities do not die out. It should be mentioned here that Mavridis and Shroff [25] suggested that the stability of the interface can be evaluated through the difference in *SR* (recoverable shear), for both coextruded layers ($\Delta S_R = S_{R,1} - S_{R,2}$) which can locally quantify shear elasticity differences (generated by pure

shear flow) between adjacent layers according to the shear stress state of the interface. On the other hand, *TNSD* can globally (in bulk) quantify the flow history and layer stretching in the merging area, where mixed shear and extensional flow occur together. Therefore, the instability onset criteria based on *TNSD* and ΔS_R are in principle different [A12].

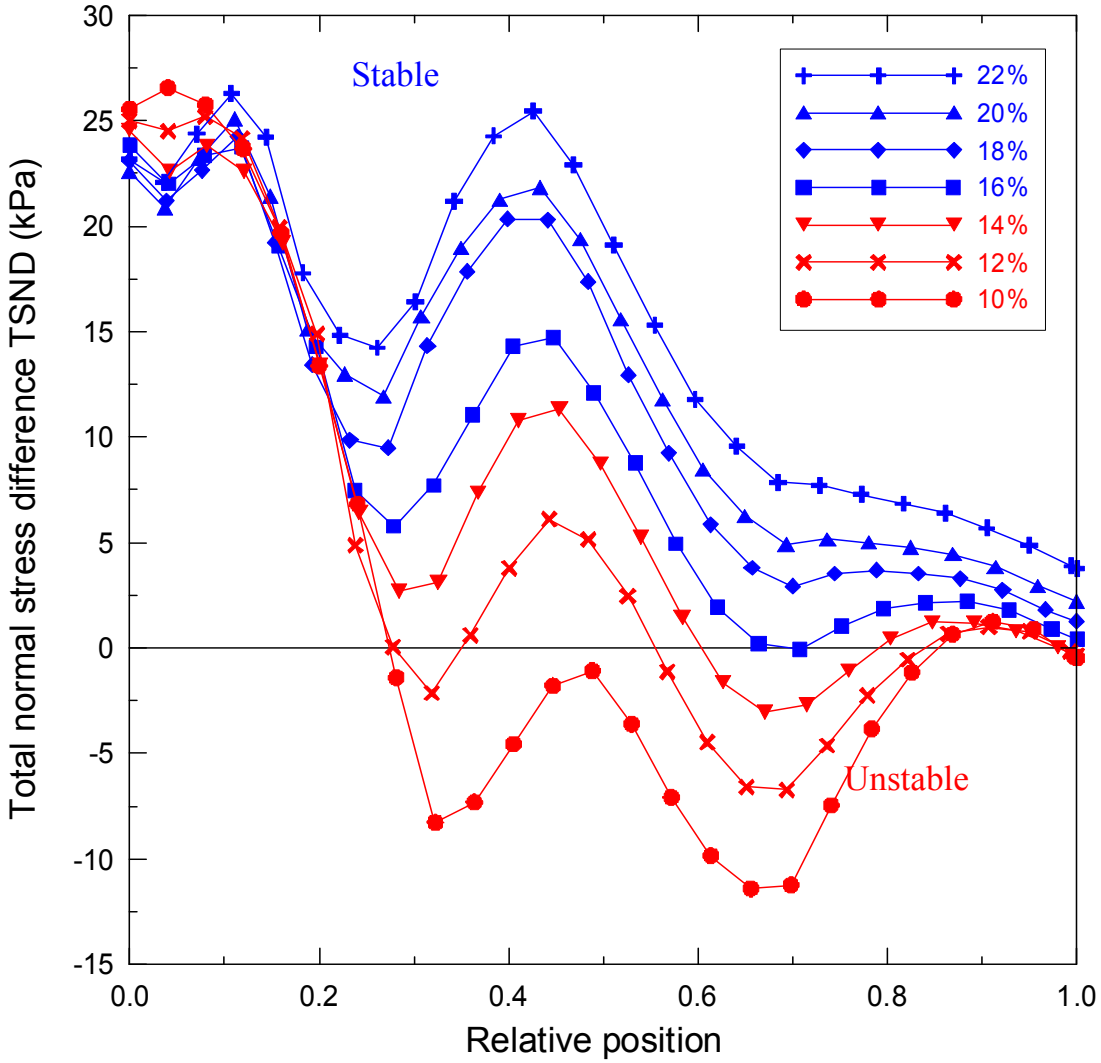

Figure 5. Comparison of the predicted *TNSD* vs. relative position along the interface for stable (minor layer 16-22%) and unstable (minor layer 10-14%), flow situations [28, A12]. © Society of Plastics Engineers. Reprodued by permission of Society of Plastics Engineers. Permission to reuse must be obtained from the rightsholder.

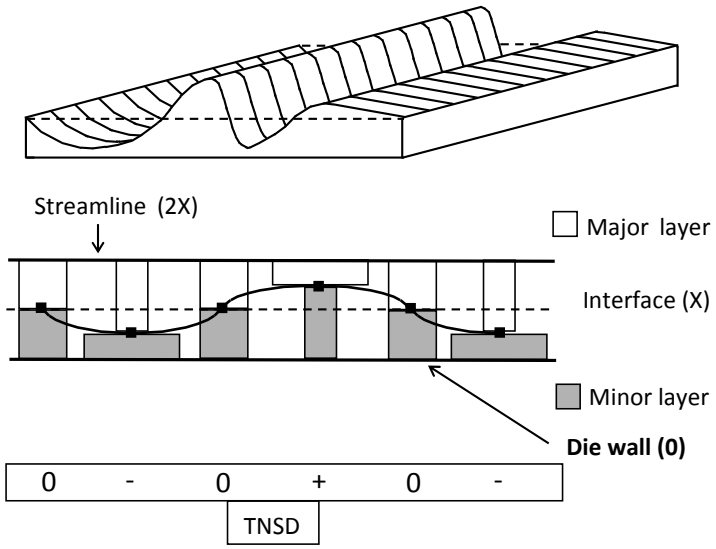

Figure 6. 3D and 2D unstable interface shape under elastic after-effect (*TNSD* changes sign) [28, A11, A12]. © John Wiley and Sons. Reproduced by permission of JohnWiley and Sons. Permission to reuse must be obtained from the rightsholder.

The analysis of the wavy unstable coextrusion flow in the merging area has been analyzed experimentally by the help of the tracer inside the coextrusion flow visualization cell having 90 degree entrance angle (Figure 8a) [36]. The sequence of the different position of the tracer during the flow in the merging area is depicted in Figure 8b)-8i). As visible from Figures 8b)-8d), intensive stretching occurs in the merging area with breaking melt stream (Figure 8e) with consequent rotation movement, believably due to intensive shearing, in the die land area (Figures 8f-8i). This intensive stretching of the minor layer with consequent rotation due to shear can explain the source of the wave instabilities as well as TNSD concept for its detection.

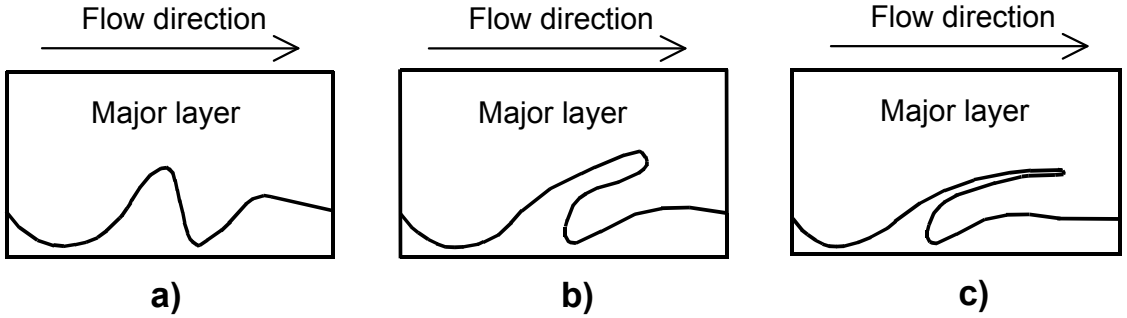

Figure 7. Mechanism of the wave instability propagation in the merging area proposed in [A12]. **7a)** Creation of the wave due to elastic after-effect. **7b)**, **7c)** Stretching of the wave due to velocity rearrangement.

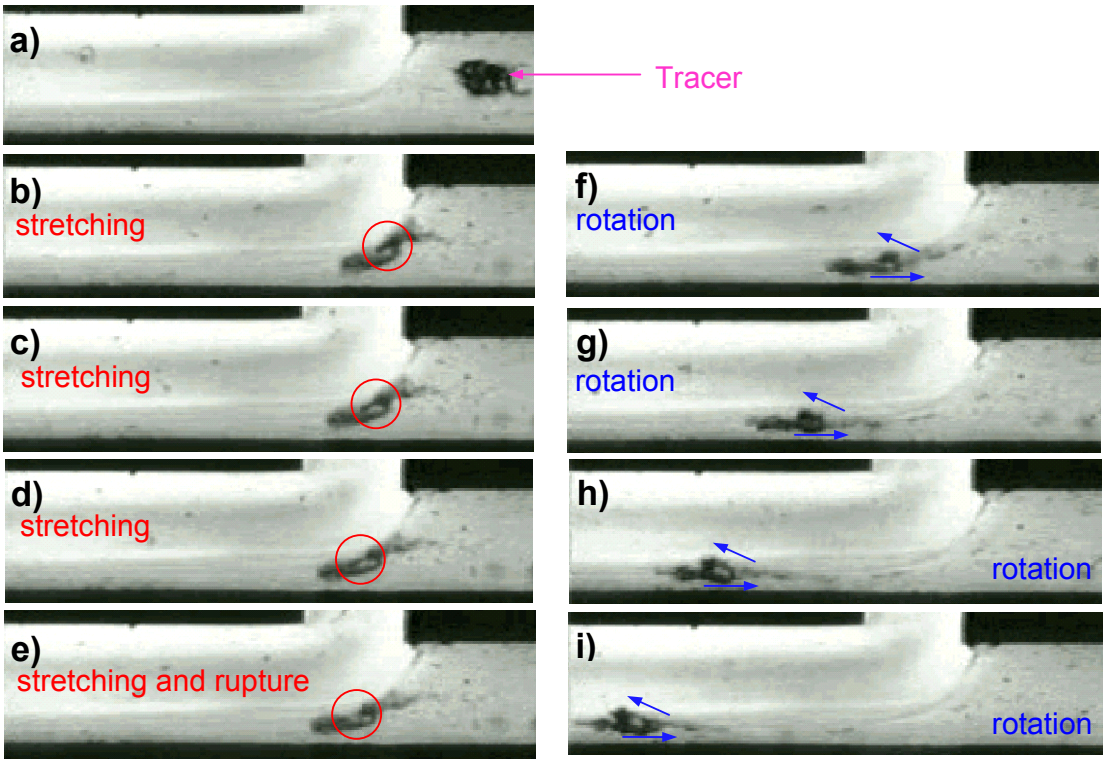

Figure 8. Flow of the tracer in the merging area of the 90 degree coextrusion visualization cell with following stages [36, A13]: **8a)** Trace shape before merging. **8b)**-**8e)** Intensive stretching of the tracer. **8f)**-**8i)** Rotation movement of the tracer. © Society of Plastics Engineers. Reprodued by permission of Society of Plastics Engineers. Permission to reuse must be obtained from the rightsholder.

The effect of die design and extensional rheology of coextruded polymer melts on the wave type of interfacial instabilities has been investigated theoretically by using TNSD sign criterion in [A11]. It was revealed that die design allowing minimization of layer stretching at the merging area suppress the wave type of interfacial instabilities. These theoretical predictions were consequently verified experimentally [37-40, A10, A14]. Additionally, for coextrusion of two different materials, it has been shown theoretically as well as experimentally, that if the extensional strain hardening in the minor layer decreases or increases, the system becomes more stable or unstable, respectively [30, A11, A13]. From the optimal resin point of view, coextruded materials with extensional thinning and no strain hardening should be preferred for coextrusion. Furthermore, the material with the lower extensional viscosity should be introduced into the minor flow and that with the higher extensional viscosity into the major layer.

4.1.2 Die exit region, zig-zag interfacial instabilities and the role of polymer processing aids

Zig-zag interfacial instabilities have been studied in [32-34, A20-A21] for mLLDPE/HDPE/mLLDPE on a Collin laboratory 3-layer coextrusion blown film line equipped by a flat spiral die system. The effect of the process aids (fluoropolymer based materials) on the zigzag type of interfacial instabilities in coextrusion flows has been investigated theoretically via viscoelastic finite element method (FEM) simulations as well as experimentally. New slip model based on 'effective continuum method' for description of the slip was developed and used for the theoretical investigation. It was revealed that Zig-zag interfacial instabilities can be suppressed by adding fluoropolymer based Polymer Processing Aids (PPA) to the outer layers due to the occurrence of slip between mLLDPA and the PPA coated die wall, because in this case the PPA particles migrates toward the die wall. It reduces the stress state on the interface as well as stretching of the thin minor layer significantly and according to the critical stress theory and TNSD concept, this is suppressing interfacial instabilities. On the other hand, if the PPA is used in all of the three layers or just in the middle layer, the PPA in the middle layer (HDPE) do not migrate towards the die wall because this layer is bounded by two moving interfaces and not by static die walls. In such case the PPA particles migrate toward the interfaces and they are flowing together with the HDPE. In this case, the utilized PPA type together with HDPE behaved as extensional stress generator rather that stress dissipater because the extensional viscosity for HDPE+PPA was found to be higher than for HDPE. Thus, at the end of the converging section, a high stress state around the interface is generated. Because the stress state on the interface is increased in this case, the situation is more dangerous from interfacial instability point of view.

The viscoelastic stress field calculation reported in [33, A21] revealed that the maximum stress appears at the end of the converging section as result of the both, shear and extensional flow components, i.e. the stress is non-monotonic along the interface in this region. Thus, the interface is stretched not only in the merging area as shown in Chapter 4.1.1 but also in the convergent section at the end of the die. As the result, zig-zag interfacial instabilities (known to be linked with the end of the die) can also be caused by intensive layer stretching according to the TNSD concept [A11-A12] with possible layer breakage similarly as in the case of wave interfacial instabilities. Smaller residence time in the convergent section compared to the merging area, can explain why zig-zag instabilities have a much lower amplitude and higher frequency than wave type instabilities; the zig-zag instabilities have no time to fully

develop themselves. This explanation may justify the use of the TNSD concept also in the case of the zig-zag interfacial instabilities. This hypothesis has recently been supported by the finding that the critical total stress value on the interface for the onset of zig-zag instabilities determined at the convergent section at the die exit region corresponds very well with the critical condition needed for the onset of wave type of interfacial instabilities in the merging are area as reported in [A10, 29]. This suggests the both types of interfacial instabilities have the same source.

4.1.3 Development of interfacial instabilities in cast film and film blowing of LDPEs

Another point of view of the assessment of interfacial instabilities is the technology where they appear. The development of interfacial instabilities in a flat coextrusion die was investigated through continual reduction of the minor layer thickness at constant output mass flow rate in [A9]. Figure 9 shows the general trend of this process for LDPEs.

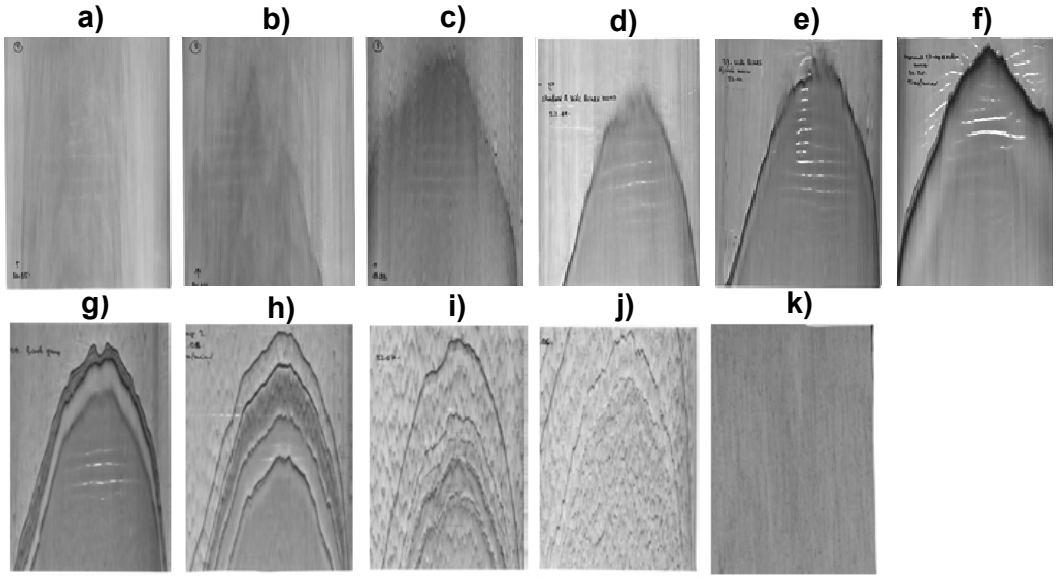

Figure 9. Development of LDPEs interfacial instabilities with minor layer being reduced [A9]. (W – wave, ZZ – zig-zag instabilities): **9a)** Stable. **9b)-9e)** Wave (W1). **9f)** Pronounced wave (W2). **9g)-9i)** Multiple waves+zig-zag (W3+ZZ). **9j)** Destroyed waves+zig-zag (W4+ZZ). **9k)** Stable (no material in minor layer). © John Wiley and Sons. Reproduced by permission of JohnWiley and Sons. Permission to reuse must be obtained from the rightsholder.

When the minor layer is thick enough, the flow is stable (Figure 9a). As the mass flow rate in the minor layer decreases, the wave instabilities start to appear in the film. They are first weak, poorly developed, but when the minor layer is still thinner, their contours become sharper, better visible (Figure 9b-9f). A further reduction of the layer causes the development of other waves inside the original one; the wave multiplies and penetrates the film thickness (Figure 9g). Then zig-zag instabilities appear gradually in the whole film area (Figure 9h-9i). With minimized minor layer the wave instabilities become significantly destroyed (Figure 9j). Finally, for a very thin minor layer, the flow becomes “stable” again (Figure 9k). The reason for this is probably that there is practically no material in the layer and instead of coextrusion a single-layer extrusion starts.

As it can clearly be seen, waves start before zig-zag instabilities, for a thicker layer. In other words, zig-zag instabilities start at more severe conditions. Thus, from the production point of view, zig-zag instabilities are not so important for the cast film technology because the product is damaged as soon as the waves start. This can be explained by the fact that in the flat die (cast film), the temperature of the material is higher (230 –270°C), that is, the shear viscosity is lower, which results in lower shear stresses. That is why the critical shear stress is hardly reached at the end of the die and the first type of interfacial instabilities to appear is waves. In film blowing die, on the other hand, the temperatures are much lower (about 190°C), which causes higher shear stresses, so the critical shear stress is easily reached and zig-zag instabilities are set before the waves as shown in [21].

4.2 Film blowing instabilities

Film blowing is technology for production of thin polymer films at which polymer melt is extruded through the annular die to form the bubble which is simultaneously inflated by the internal bubble pressure, stretched by the nip rolls and cooled down by the surrounding air [44-45], see Figure 10a. The main purpose of the film blowing process is to produce a stable film with good physical and optical properties at a maximum production rate. However, there are different film blowing instabilities which can take the place between die and freezeline height and lead to production of large amounts of film scrap, reduction of film production-rate and film of inferior quality (nonuniform mechanical/optical properties) [46-49], see Figure 10b.

Due to complexity of the process, mainly caused by strongly non-isothermal conditions at which polymer melt viscoelasticity is highly non-

linear, the role of die design, processing conditions and polymer melt rheology on the process stability is not fully understood yet. In order to understand the film blowing process and its stability in more detail, firstly, variational principles were employed to develop novel model describing the formation of the bubble, due to internal bubble pressure and take-up force, in such a way that the resulting bubble shape satisfies the minimum energy requirements. The derived equations for the bubble shape (including HDPE wine-glass shape), take-up force and internal bubble pressure have simple analytical forms with only several physical parameters [A22-A23].

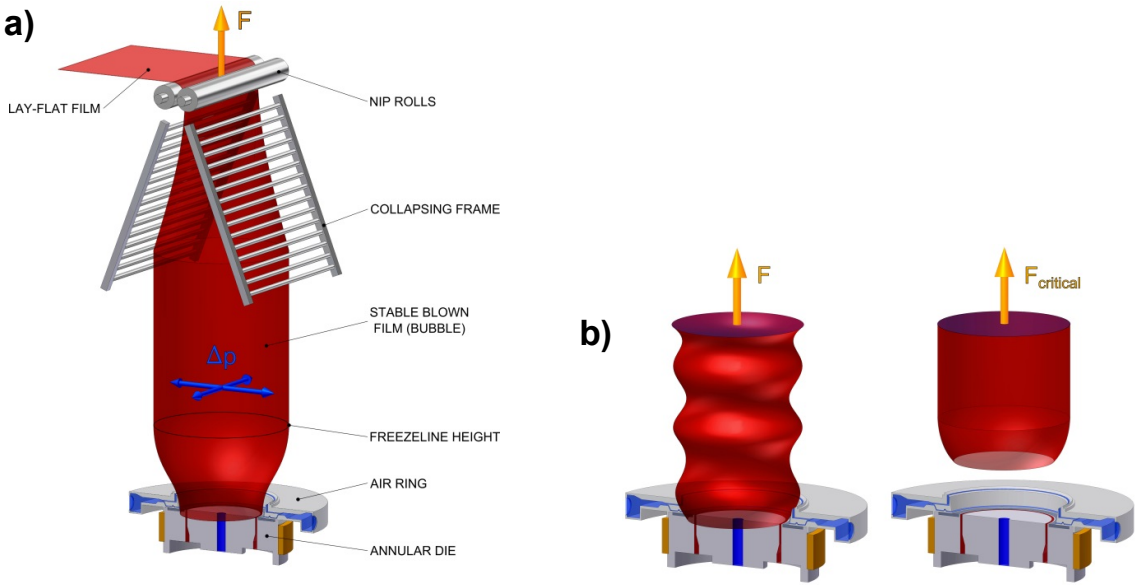

Figure 10. Film blowing process. **10a)** Stable case [A18]. **10b)** Draw resonance and bubble tear instabilities affected by the forces, F, and $F_{critical}$, respectively, where $F < F_{critical}$ [A19]. © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

Secondly, the proposed variational principles based film blowing model has been generalized considering nonisothermal conditions and non-Newtonian behavior of polymer melts and its predictions were compared with both, theoretical and experimental data (internal bubble pressure, take-up force, bubble shape, velocity and temperature profiles) taken from the open literature [A17]. For this purpose, recently proposed generalized Newtonian model depending on three principal invariants of the deformation rate tensor, *D*, and its absolute value defined as square root of D*D, has been used [A16]. It has been found that film blowing

model predictions are in very good agreement with the corresponding experimental data. Thirdly, having realistic film blowing model, a numerical stability analysis of the film blowing process has been performed utilizing physically limiting criteria (maximum tensile and/or hoop stress) to investigate the complex relationship between processing conditions (internal bubble pressure, heat transfer coefficient, mass flow rate, cooling air temperature, melt/die temperature), material parameters (rupture stress, Newtonian viscosity, flow activation energy, power law index) and film blowing stability [A18]. It has been shown that the melt/die temperature has the highest impact on the film blowing stability window size as well as on the maximum and minimum achievable film thickness. In more detail, it has been found that processing parameters together with flow activation energy have much higher effect on the film blowing stability and maximum achievable film thickness than the basic rheological characteristics of the polymer melt. On the other hand, the effect of basic rheological parameters of the polymer melt become much more important than processing parameters (except of melt/die temperature) in order to reach minimum film thickness. Finally, the role of extensional rheology, the most important material characteristic for shear free flows, on the film blowing process stability has been investigated in [A19]. It has been revealed experimentally as well as theoretically that the relationship between film blowing stability window size (and/ or minimum achievable final film thickness) and extensional strain hardening is of non-monotonic character for a given range of melt strengths, i.e. there exists some optimal values for both variables to reach maximum stability window size and/or the smallest minimum achievable final film thickness. Based on the theoretical investigation, it has been revealed that the film blowing stability increases (or minimum achievable film thickness decreases) if the melt strength, σ, increases with the increased ratio of maximum steady state uniaxial elongational viscosity divided by three times of Newtonian viscosity, $\frac{\eta_{\mathrm{E,max}}}{3\eta_0}$, more than according to the following simple relationship: $\sigma = A'\left(\frac{\eta_{\mathrm{E}}}{3\eta_0}\right)^2 + B'\left(\frac{\eta_{\mathrm{E}}}{3\eta_0}\right) + C'$, where A', B' and C' are constants. It also has been revealed that there is always some minimum melt strength value for the given $\frac{\eta_{\mathrm{E,max}}}{3\eta_0}$ at which the film blowing stability is maximized or at which the achievable final film thickness is at its minimum. It has been concluded that the proposed variational principle based model can describe quantitatively as well as qualitatively the experimentally

determined film blowing stability contours for linear as well as branched polyolefins.

Another frequent problem in the production of metallocene linear low-density polyethylene (mLLDPE) films by the film blowing process is the occurrence of flow instabilities initiated inside or just at the end of the extrusion dies (sharkskin, degradation), which limit the production rate and decrease the product quality. If such problems arise, the question is what causes these phenomena and how they can be avoided. With the aim of understanding these problems flow behavior of two different mLLDPEs was determined and used for the process simulation [A24]. It was shown that the capillary-rheology data together with 2D finite element method can be used for the prediction of sharkskin phenomenon as well as degradation of mLLDPE melts. Moreover, non-isothermal, viscoelastic 3D FEM analysis of the film blowing flat spiral die performed in [A25] revealed that improper die design can cause localized intensive shearing and viscous heating of the polymer melt, which can destabilize the flow inside the die considerably.

4.3 Die Drool Phenomenon

Die drool phenomenon is unwanted accumulation of a material at the die exit during polymer melt extrusion [50-53, A26-A32], see Figure 11. Due to high temperature and oxygen in the air, the accumulated material degrades and after certain time, it is removed from the die exit by moving extrudate, which negatively influences final optical/electrical or mechanical properties of the final product, which is undesirable. In order to extend the knowledge in this area, the effect of die design, processing conditions, polymer type on the die drool phenomenon has been investigated experimentally by using specially designed annular extrusion die depicted in Figure 12 as well as theoretically by using viscoelastic finite element method employing a modified White–Metzner model as the constitutive equation [A26-A31].

In the case of narrow molecular weight metallocene-based LLDPE [A26-A27], it has been found that there exists a critical negative pressure at the die exit region, which cause a significant suction effect in the polymer melt explaining the onset of the die drool phenomenon. The pressure, magnitude of the pressure gradient and normal pressure gradient components were revealed to be variables allowing assessment of die drool phenomenon intensity with respect to given processing conditions and die design.

In the case of broad molecular weight HDPE [A28-A31], it has been revealed that the long-chain branching, low polymer melt elasticity and

shear viscosity significantly reduce die drool phenomenon at the die exit region. It has been concluded that die drool phenomenon of HDPE polymer melts can be explained by the flow induced molecular weight fractionation.

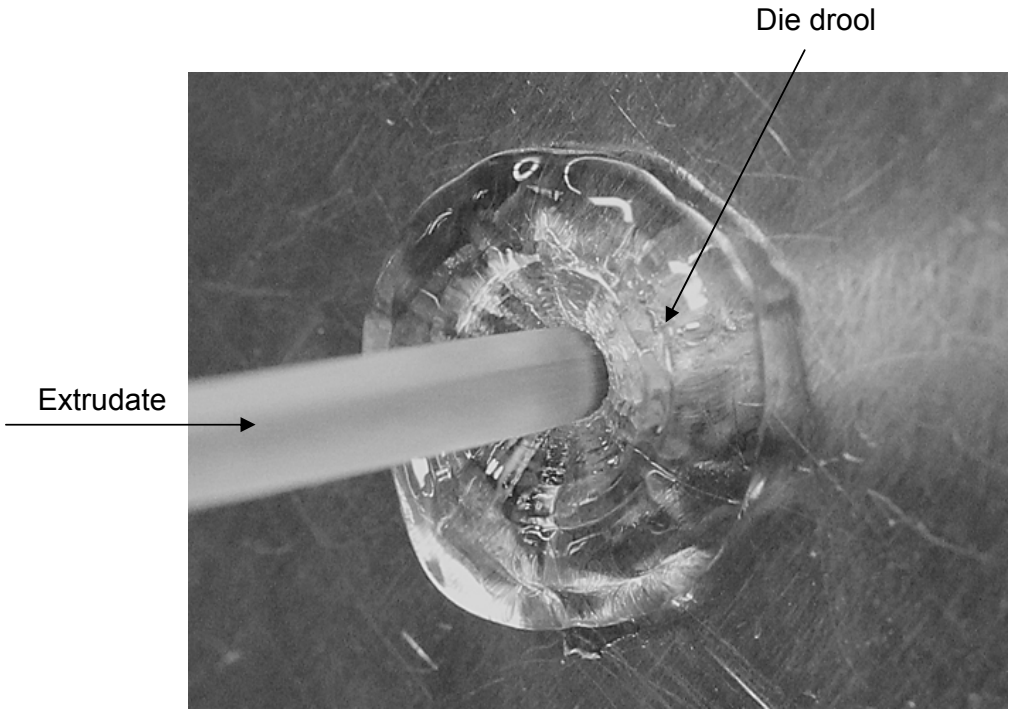

Figure 11. Die drool phenomenon for HDPE polymer melt [A31]. © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

It has been found that first, onset as well as intensity of slip–stick instability and flow induced molecular weight fractionation are in direct relationship, i.e., low molecular weight polymer chains start to fractionate from the main polymer melt stream at the onset of slip–stick flow regime initiating formation of low viscosity layer at the die wall, which leads to its consequent unwanted accumulation at the die lips – die drool phenomenon. Second, due to enhanced melt elasticity (by the presence of long linear chains of linear HDPE polymer), the flow induced molecular weight fractionation is more effective which results in narrow molecular weight distribution of die drool sample containing small amount of long chains. Third, buildup ratio sensitivity to apparent shear rate is the highest in the slip–stick regime and its value increases with increased content of very long chains. Fifth, the flow induced molecular weight fractionation takes place only in a very thin layer near the die wall (i.e., within less than 8% of the channel radius for the studied processing

conditions and HDPE polymer samples). Finally, the effect of flared length and die exit angle on the internal die drool intensity during extrusion of HDPE has non-monotonic character. It has been suggested that suppression mechanism of the internal die drool phenomenon through die exit modification can be understood through the balance between the melt pressure/normal stresses at the die exit, adhesion at metal wall/flowing melt interface and extensional stress induced by the extrudate draw off, which can lead to flow situation at which low molecular weight species are effectively removed from the die exit region by the moving extrudate and only small portion of them remains at the die exit face. Current stage of knowledge in area of die drool phenomenon in plastics extrusion is summarized in our recently published review paper [A32].

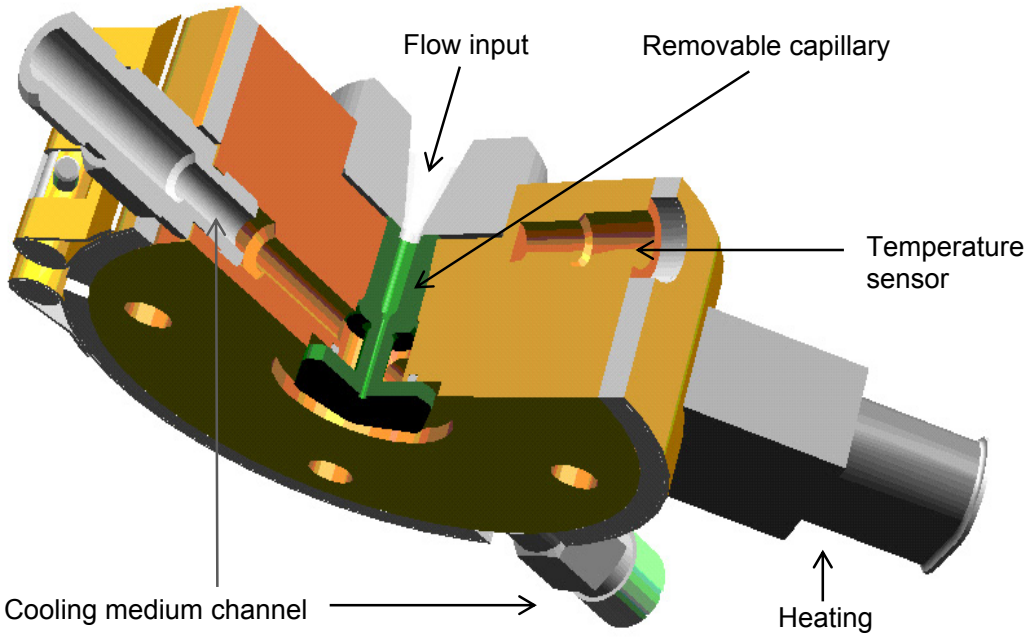

Figure 12 Special annular extrusion die utilized for die drool phenomenon investigation [A26]. © John Wiley and Sons. Reproduced by permission of JohnWiley and Sons. Permission to reuse must be obtained from the rightsholder.

5 Applied rheology for production and characterization of polymeric nanofiber based filters

Polymeric nanofibers for filtration purposes can be produced by the free surface electrospinning technology at which electrical forces are utilized to draw polymer solution jets into fine fibers [54]. This technology allows the ejection of multiple polymer jets from the surface of electrically charged rotating electrode to reach high nanofiber productivity [55-57]. In order to reach stable production of nanofibers (i.e. quality/property/homogeneity characteristics of the produced nanofibres are not changed during the time), the process must be optimized. In our patent [P2], it was shown that rheological analysis of the polymer utilized in electrospinning process can be used to optimize electrospinning process and increase its efficiency. In this case, the optimized PUR nanofibers production was achieved by utilization of stirring polymer solution with constant rheological relaxation spectra for which the polydispersity index was not changed considerably during the electrospinning process.

Characterization and prediction of structure/property of polymeric nanofiber based filters is very challenging task mainly due to problematic manipulation with extremely small fibers and highly sensitive apparatus requirements for nanoweb sample testing [54, 58-59]. In order to evaluate their basic tensile characteristics, specific methodology utilizing the rotational rheometer equipped with Sentmanat extensional rheometer was proposed and successfully used for nanofiber based PUR nonwovens produced by electrospinning technology [A33] (see Figure 13).

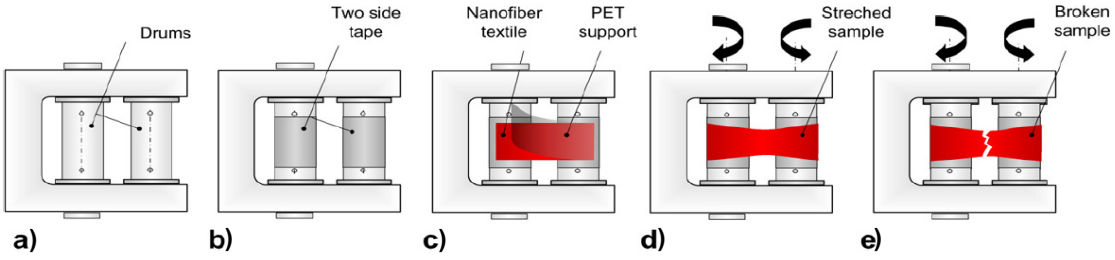

Figure 13 Visualized methodology for the tensile testing of the nanofiber nonwoven by using Sentmanat extensional rheometer [A33]. **13a)** SER unit. **13b)** SER with double-sided adhesive tape. **13c)** Nanofiber web deposition on the SER unit. **13d)** Sample stretching. **13e)** Sample at break. © Elsevier. Reproduced by permission of Elsevier. Permission to reuse must be obtained from the rightsholder.

Main advantage of this ‘rheology based’ methodology is possibility to measure very fine structures with low enough experimental error due to utilization of very high sensitive torque/normal force transducers, which are normally present on standard rotational rheometers for polymer melt rheology evaluation. Moreover, the measurements can be done at different extensional strain rates and temperatures by using the conventional rheometer oven which is difficult or impossible by using standard methodologies.

In order to predict gas filtration characteristics of polymeric nanofiber based filters, novel 3D model has been proposed and successfully tested for PUR filters prepared by electrospinning technology [A34-A35]. The proposed model considers slip/transition/free molecular flow regime, Brownian diffusion, particle–polymeric fiber interactions, aerodynamic slip and sieve. It is important to mention that shear viscosity of the gas is modeled as the non-Newtonian fluid with respect to the Knudsen number which becomes very high when gas is flowing around the polymeric nanofibers.

6 Conclusion remarks

This thesis provides overview of our research in area of applied rheology in polymer science. The main findings in this research field are summarized below.

- Innovative method for determination of the uniaxial extensional viscosity from the measured entrance pressure drop of orifice dies has been introduced and the role of the temperature/pressure on the melt rheology has been estimated.
- Advanced constitutive equations discriminating between different topologies of polymers have been developed for realistic description of their flow behavior during polymer processing.
- Advanced viscoelastic finite element modeling and novel criteria allowing prediction of interfacial instability onset in coextrusion have been proposed. Variational and minimum energy principles based model allowing modeling of free surface flow instabilities in film blowing has been developed. Negative pressure at the die exit and flow induced molecular weight fractionation have been discovered as the key factors explaining die drool phenomenon occurring during the polymer melt extrusion process.
- Novel rheology based methodologies have been introduced to optimize production of polymeric nanofibers as well as to characterize nanofiber based filters based on the newly proposed 3D model allowing to model slip around the polymeric nanofibers considering ‘non-Newtonian’ character of the filtered media.

It can be stated that the results presented in this thesis contributed significantly to the current stage of knowledge in area of applied rheology for polymers.

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8 List of publications and patents comprising the DSc. Thesis (corresponding author denoted by *):

Number of papers: 35
Number of papers (applicant first author): 17
Number of papers (applicant corresponding author): 33
Number of citations without self-citations (10.3. 2014): 233
2012 impact factor of all papers: 59.284
Average 2012 impact factor per paper: 1.694
Number of patents: 2

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Statement about the authorship of the presented research results: In the majority of the presented research results the contribution of the author of this Thesis was pivotal, contributing by development of the theories, models, numerical schemes and their computer implementation, performing experimental measurements, data processing and interpretation, suggesting and developing novel experimental methodologies as well as supervising of Ph.D. students during their research work (Kateřina Chaloupková, Radek Pivokonský, Roman Kolařík, Jan Musil and Wannes Sambaer). This is reflected by the fact that he was the corresponding author of 33 publications and the first author of 17 publications (with overlap).

9 Scientometric data for M. Zatloukal

Date: 7.3. 2014
Number of publications registered in Web of Science: 88
Total number of citations: 461
Average Citations per Article: 5.84
H-index: 12

Web of Science ResearcherID:
http://www.researcherid.com/rid/H-6347-2012

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