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SIMULATION OF POLYMER CRYSTALLIZATION: ROLE OF THE VISCO-ELASTICITY

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ABSTRACT

In polymer processing, it is established that the flow causes the polymer chains to stretch and store the energy, by changing their quiescent state free energy. Koscher et al. [1] presented in 2002 an experimental work concerning the flow induced crystallization. They made the assumption that the polymer melt elasticity, quantified by the first normal stress difference, is the driving force of flow-induced extra nucleation. In their work, a constant shear stress is considered, and the first normal stress difference agrees with the use of the trace of the stress tensor.

The stored energy due to the flow " ΔGe " is commonly called elastic free energy and associated to the change in conformational tensor due to flow. By extending the Marrucci theory [2], several studies link this ΔGe to the trace of the deviatoric stress tensor (first invariant). In this paper, a numerical model able to simulate polymer crystallization is developed. It is based on the assumption that flow induced extra nucleation is linked to the trace of the deviatoric stress tensor. Thus a viscoelastic constitutive equation, the multimode Upper Convected Maxwell (UCM) model, is used to express the viscoelastic extra-stress tensor τ^{VE} , and a damping function is introduced in order to take into account the nonlinear viscoelasticity of the material. In Koscher's work [1], the

integral formulation of the Upper Convected Maxwell (UCM) model is used too, but without any damping function, i.e. they assume that the polymer behaves as linear viscoelastic.

As an application, a 2D isothermal flow configuration between two plates is simulated. A comparison between the proposed model and the Koscher's one is then performed, and interesting results are presented: without introducing a damping function, the two models give similar results in the same configurations, but the introduction of a damping function leads to important discrepancies between the two models, seeming that the assumption of a linear viscoelastic behavior is not realistic when the fluid strain and /or stresses are greater than a given values.

Keywords : Crystallization, Flow induced nucleation, Polymer, Viscoelasticity

1. INTRODUCTION

To simulate the heat transfer in polymers materials during their processing in an accurate way, it is necessary to take into account all the thermodynamical and physical transformations. One of them, which concern specifically the semicrystalline polymers, is the crystallization phenomenon.

The thermomechanical history of polymers affects their crystallization kinetics during their processing. The shear stress modifies both the crystallization morphology and kinetics. It orients the macromolecular chains, which helps the nucleation, accelerates the crystallization and generates oriented morphologies. We can summarize the effects of shearing stresses on the crystallization as follows:

- acceleration of the crystallization kinetics;
- increase in the number of nuclei, resulting in a decrease of the size of crystallites;
- orientation in the deposition of nuclei in rows parallel to the direction of flow;
- increase of the anisotropy of the crystalline lamellae;
- increase of the crystallization temperature and decrease of the induction time.

Several studies concerning the flow induced crystallization can be found. Usually, they aim to find a set of simple and experimentally accessible parameters to describe the crystallization kinetics. Several authors have modeled the flow effect on the crystallization kinetics using the isokinetic Nakamura equations. The models obtained account for the relative crystallinity evolution without describing the crystalline morphology.

One can quote the work of Guo et al. [3], which links the flow effect on the crystallization kinetics to the increase of the equilibrium melting temperature T_m^0 in the Nakamura model. For a more detailed review on crystallization kinetics modeling, see [4].

Two types of approaches were employed during the development of the global theories of crystallization kinetics: the geometrical approach, which express the volume occupied by the semicrystalline entities, and the probabilistic approach, which calculates the probability that an element of volume is transformed. The main differences lie in the mathematical treatment, but the basic assumptions and especially the results are identical.

The geometrical approach considers the free growth of crystalline entities of simple geometries, and then applies a correction taking into account the so-called impingement (i.e. the fact that the growth of each entity is not free, but blocked by the contact with the closest entities).

For a finite volume, the variation of the crystallinity $d\alpha$ is related to the variation of the crystallinity for an infinite available volume $d\alpha'$ by:

$$d\alpha = (1 - \alpha) \cdot d\alpha' \quad (2)$$

This expression can be integrated over time and gives:

$$\alpha(t) = 1 - \exp(-\alpha'(t)) \quad (3)$$

α' is a fictitious crystallinity, obtained for a free growth of the crystallites. Equation (3) represents the basis of all the Avrami type models.

In the probabilistic approach, Kolmogorov [5] and Evans [6] chose to calculate the probability that a representative point of a volume is crystallized. They assume that, within a good approximation, this probability represents the crystallinity $\alpha(t)$. Billon in [7] showed that the two theories of Evans and of Avrami are equivalent because they are implicitly based on the same assumptions. In this work, the global approach of Avrami is used.

A variety of approaches have been proposed to model the flow effect on crystallization kinetics. The most interesting ones explicitly take into account the nucleation and growth process. Indeed, experimental observations have clearly shown that the number of nuclei per unit volume (or nucleation density) is considerably increased under shear conditions [8,9]. This additional nucleation rate can be linked to various parameters: free energy related parameters [10], shear rate [11], combination of the shear strain and the shear rate [12], recoverable strain tensor [13].

Koscher et al. [1] carried out a consequent experimental work to characterize the flow-induced crystallization kinetics of an isotactic polypropylene. The samples were melted in a Linkam shearing device (plate-plate geometry), brought to the wanted crystallization temperature and subjected to short term shearing treatments (up to 100 seconds) at various shear rates. The subsequent crystallization was then observed using polarized light microscopy. It was shown that the number of nuclei and thus, the rate of crystallization, are dramatically raised by the increase in shear rate. The corresponding kinetic model, based on the Avrami theory, connects the extra number of activated nuclei to the first normal stress difference induced by the shear treatment. The stress tensor is calculated according to a viscoelastic Maxwell model, leading to a semi-analytical expression of the degree of crystallinity in the case of an isothermal pure shear flow. This model, in its current form, doesn't predict the formation of oriented crystallites, but it takes into account the link between the rheological behavior of the melt and the crystallization kinetics enhancement.

It is established that the flow causes the macromolecular chains to stretch and store additional energy, resulting in an increase in the melt free energy. The quantity of stored energy is commonly called elastic free energy (ΔG_e) and is related to the flow-induced change in conformational tensor. Extending the Marrucci theory [2], several studies link ΔG_e to the trace of the extra-stress tensor, see the recent review by Mazinani et al. [14] for instance. In Koscher's work [1], the assumption is made that the polymer melt elasticity, quantified by the first normal stress difference, is the driving force of flow-induced extra nucleation. They consider a pure shear flow, in which the first normal stress difference is equivalent to the trace of the extra-stress tensor.

Using the experimental data presented by Koscher et al. [1], we develop, in the present paper, a numerical model able to simulate the crystallization of polymers. We make the

assumption that the polymer melt elasticity, quantified by the trace of the extra-stress tensor is the driving force of flow-induced extra nucleation. In the case of pure shear flow, this assumption agrees with Koscher's approach of considering the first normal stress difference as the enhancement factor. Thus, the sensitivity of the crystallization kinetics to the flow is not only a consequence of the flow kinematics, but is determined by the rheological behavior of the melt.

2. MATHEMATICAL FORMULATION

2.1. Balance Equations

In the general compressible and non-isothermal case, modelling the polymer melt flow requires a coupling between the mass conservation or continuity equation (1), the momentum equation (2) and the energy equation written in the temperature form (3):

$$\frac{\partial \rho}{\partial t} + \rho \nabla \cdot \mathbf{v} = 0 \quad (1)$$

where ρ is the density and \mathbf{v} the velocity vector;

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p \mathbf{I} + \nabla \cdot \boldsymbol{\tau}^V + \rho \mathbf{f} \quad (2)$$

where p is the hydrostatic pressure, \mathbf{I} the identity tensor, $\boldsymbol{\tau}^V$ the viscous extra-stress tensor and \mathbf{f} the specific body forces vector;

2.2. Crystallization Kinetics

Polymer crystallization can be described as a nucleation and growth process: nuclei are activated and grow into crystallites at rates depending on the thermo-mechanical state of the molten polymer.

The spherulitic growth process is modeled using two sets of Schneider rate equations [24], i.e. one set for each type of nucleation:

$$\left\{ \begin{array}{l} \frac{\partial \varphi_3^{T,f}}{\partial t} + \mathbf{v} \cdot \nabla \varphi_3^{T,f} = 8\pi \dot{N}^{T,f} \quad (\varphi_3^{T,f} = 8\pi N^{T,f}) \\ \frac{\partial \varphi_2^{T,f}}{\partial t} + \mathbf{v} \cdot \nabla \varphi_2^{T,f} = G_T \varphi_3^{T,f} \quad (\varphi_2^{T,f} = 4\pi R_{tot}^{T,f}) \\ \frac{\partial \varphi_1^{T,f}}{\partial t} + \mathbf{v} \cdot \nabla \varphi_1^{T,f} = G_T \varphi_2^{T,f} \quad (\varphi_1^{T,f} = S_{tot}^{T,f}) \\ \frac{\partial \varphi_0^{T,f}}{\partial t} + \mathbf{v} \cdot \nabla \varphi_0^{T,f} = G_T \varphi_1^{T,f} \quad (\varphi_0^{T,f} = V_{tot}^{T,f}) \end{array} \right. \quad (4)$$

It should be noticed that the Schneider rate equations are mathematically equivalent to the generalized Kolmogorov formulation [15], which is itself the basis of the Avrami-Nakamura theory. In these sets of equations, convective terms are necessary to take into account the advection of crystallinity by the flow. The superscript "T" denotes thermally induced

crystallization, whereas the superscript "f" denotes flow induced crystallization. For more details, see [15]

The extended global crystalline volume fraction φ_0^{global} is simply the sum of the thermally induced extended crystalline volume fraction and the flow induced extended crystalline volume fraction:

$$\varphi_0^{global} = \varphi_0^T + \varphi_0^f \quad (5)$$

The real global crystalline volume fraction (or the relative crystallinity) α is finally obtained using the Avrami model for spherulitic impingement:

$$\alpha = 1 - \exp(-\varphi_0^{global}) \quad (6)$$

2.2.1. Thermally Induced Nucleation

A logarithmic variation of the density of thermally activated nuclei N^T with the degree of supercooling $\Delta T = T_m^0 - T$ (T_m^0 being the equilibrium melting temperature) is assumed [16]:

$$\ln(N^T) = b\Delta T + d \quad (7)$$

where b and d are material parameters to be determined experimentally. More details are given in [17].

2.2.2. Flow Induced Nucleation

As discussed in the introduction, the connection between the flow characteristics and the enhancement of nucleation have been described by various phenomenological models, using a more or less easily experimentally accessible variable, such as the shear rate, the stress tensor or an energy-based function. It is not yet possible to affirm which option is the best, mainly because the physical basis of the interaction between flow and crystallization are not completely understood. Nevertheless, the most widespread explanation is that flow tends to orientate and stretch the macromolecular chains constituting the polymer melt, thus decreasing the entropy, increasing the local molecular ordering and the predisposition to give new homogeneous nuclei, whereas in quiescent conditions the heterogeneous nuclei are the precursors of the crystallization process. Based on these considerations, it appears clearly that a realistic flow induced crystallization model should take into account information about the macromolecular chain dynamics. This seems particularly important in the case of short-term flows: after the cessation of flow, the molecular orientation is not relaxed instantaneously but progressively: an ordered state remains for a more or less long time depending on the molecular weight distribution. As a consequence, the flow induced nucleation process can continue although the melt is not flowing anymore.

In the present paper, the first invariant of the viscoelastic extra-stress tensor $tr(\boldsymbol{\tau})$, which quantifies the elasticity of the melt and thus the molecular orientation, is used as the driving force of flow induced nucleation according to the following proposed relationship:

$$\dot{N}^f = C \left[\text{tr}(\boldsymbol{\tau}^{VE}) \right]^p \quad (8)$$

where C and p are two material-related parameters to be determined using the experimental data obtained by Koscher [18] for isotactic polypropylene.

2.2.3. Crystalline growth rate

As discussed in the introduction section, the radial growth rate of the spherulites G_T is assumed to be temperature dependent only; hence a classic Hoffman-Lauritzen [12] expression is used:

$$G_T(T) = G_0 \exp\left(-\frac{U^*}{R(T-T_\infty)}\right) \exp\left(-\frac{K_g}{T\Delta T}\right) \quad (9)$$

where U^* is a parameter similar to an activation energy of motion, R is the gas constant, $T_\infty = T_g - 30$ K is the temperature below which molecular motion becomes impossible, T_g is the glass transition temperature and ΔT is the supercooling degree. The parameters G_0 and K_g have to be determined by experiments, for instance differential scanning calorimetry (DSC).

2.3. Rheological model

Our crystallization kinetics model links the flow-induced extra nucleation to the trace of the extra-stress tensor, thus a viscoelastic constitutive equation is required to express the viscoelastic extra-stress tensor $\boldsymbol{\tau}^{VE}$. In Koscher's work [1], the rubber-like liquid (RLL) constitutive equation, also known as Lodge equation, is used without any damping function, i.e. the polymer is assumed to behave as a linear viscoelastic material:

The original Lodge equation is based on the assumption that temporary polymer network strands are deformed affinely with the macroscopic strain. However, large strains induce a change in the structure of the temporary network (Wagner 1976b). According to Wagner, there are two independent decay mechanisms for network strands:

- linear-viscoelastic (time-dependant) relaxation, related to a memory function,
- disentanglement by deformation, related to the damping function h (non-linear effects).

Hence, assuming time-strain separability, the relaxation modulus can be expressed as:

$$G(t, \gamma) = G(t) \cdot h(\gamma) \quad (12)$$

where the damping function is that proposed by Wagner [Wagner 1976b]:

$$h(\gamma) = e^{-n\sqrt{\gamma^2}} \quad (13)$$

Since the choice of the damping function does not affect drastically the rheological behavior, preference was given to a simple form in which only one material parameter n is required.

As our model, the Upper Convected Maxwell (UCM) differential formulation equivalent to the Lodge integral formulation, is introduced [2]:

$$\boldsymbol{\tau}^{VE} + \frac{1}{\lambda} \boldsymbol{\tau}^{VE} = \frac{h \cdot \eta}{\lambda} \mathbf{D} \quad (12)$$

$\overset{\nabla}{\boldsymbol{\tau}}^{VE}$ is called the upper convected derivative of the viscoelastic extra-stress tensor; it is a frame invariant quantity that can be defined as:

$$\overset{\nabla}{\boldsymbol{\tau}}^{VE} = \frac{\partial \boldsymbol{\tau}^{VE}}{\partial t} + \mathbf{v} \cdot \nabla \boldsymbol{\tau}^{VE} - \boldsymbol{\tau}^{VE} \cdot \nabla \mathbf{v} - (\nabla \mathbf{v})^T \cdot \boldsymbol{\tau}^{VE} \quad (13)$$

λ is a relaxation time and η is a viscosity. The latter is linked to the linear relaxation modulus by the following simple relationship:

$$\eta = G \cdot \lambda \quad (14)$$

A multimode description is convenient to model and characterize the relaxation spectrum using rheometry. Similarly to equation (14), a viscosity can be defined for each mode:

$$\eta_i = G_i \cdot \lambda_i \quad (17)$$

The UCM constitutive equation gives the viscoelastic extra-stress tensor corresponding to the i^{th} mode:

$$\overset{\nabla}{\boldsymbol{\tau}}_i^{VE} + \frac{1}{\lambda_i} \boldsymbol{\tau}_i^{VE} = \frac{h \cdot \eta_i}{\lambda_i} \mathbf{D} \quad (18)$$

and the total extra-stress tensor is simply the sum of the modal extra-stress tensors:

$$\boldsymbol{\tau}^{VE} = \sum_{i=1}^N \boldsymbol{\tau}_i^{VE}$$

3. APPLICATION OF THE MODEL

In this section, the general model described above is applied to a polypropylene melt in a 2D pipe flow configuration, under isothermal conditions (isothermal crystallization,). Computations are carried out using a transient numerical procedure based on finite elements method. The aim is to compare the results obtained using our model considering with a linear viscoelastic behavior (Koscher's configuration) and to those obtained with non linear viscoelastic model, by introducing the damping function.

First, a validation of the model is proposed in a simple shear flow.

4. MATERIAL DATA

An isotactic polypropylene (iPP Eltex HV 252, commercialized by Solvay) is studied. Its weight average molecular weight is $M_w = 180.8 \times 10^3$ g.mol⁻¹ and its polydispersity index is $M_w/M_n = 7.3$ (where M_n is the number average molecular weight). An in-depth characterization of this polymer has already been carried out and is available in the literature: thermophysical properties in [18,19], rheological properties and crystallization kinetics in [1].

4.1. Thermophysical Properties

All the thermophysical properties are given as a function of the liquid state and the solid state by means of mixing law, weighted by the relative crystallinity, see [17].

4.2. Rheological Properties

The viscoelastic behavior of the polymer was studied by Koscher assuming an eight-mode Maxwell model. Information about the measurement and identification procedure can be found in [20]. The values of the relaxation times and the corresponding contributions are reported in Table 1.

TABLE 1 - RELAXATION SPECTRUM OF PP FOR THE MAXWELL MODEL AT $T = 203$ °C

Mode no. i	Relaxation time λ_i (s)	Contribution G_i (Pa)
1	3.162×10^{-3}	7.796×10^4
2	1.118×10^{-2}	1.489×10^4
3	4.394×10^{-2}	1.321×10^4
4	1.638×10^{-1}	4.202×10^3
5	6.105×10^{-1}	1.279×10^3
6	2.276×10^0	2.490×10^2
7	8.483×10^0	2.541×10^1
8	3.162×10^1	5.244

In addition to the viscoelastic properties, solving the balance equations (2) and (3) requires parameters for the generalized Newtonian model. These parameters are found using the dynamic frequency sweep experiments carried out by Koscher. All the parameters of the generalized Newtonian model are listed in Table 2.

5. RESULTS

5.1. Isothermal shear flow: validation of the model

This section is devoted to the validation of our numerical model against existing experimental data and computational results, in a simple configuration: the isothermal crystallization with short-term shearing treatment at constant shear rate for the whole flow. In this configuration the trace of the extra stress tensor is identical to the first normal stress difference, so that, the comparison with Koscher's model become possible. The effects of the shearing intensity and of the temperature on crystallization kinetics are presented in Fig. 1 in terms of half-crystallization time. On one hand, the acceleration of crystallization becomes noticeable when the shear rate exceeds a value ranging between 0.1 and 1 s^{-1} : this can be considered as the critical shear rate. On the other hand, the decrease in crystallization temperature has an enhancing effect on the kinetics whatever the shear rate. In order to validate our numerical model, the results are compared to Koscher's experimental measurements [18]. The agreement is quite good.

In particular, the critical shear rate value and the half-crystallization time decrease are well predicted.

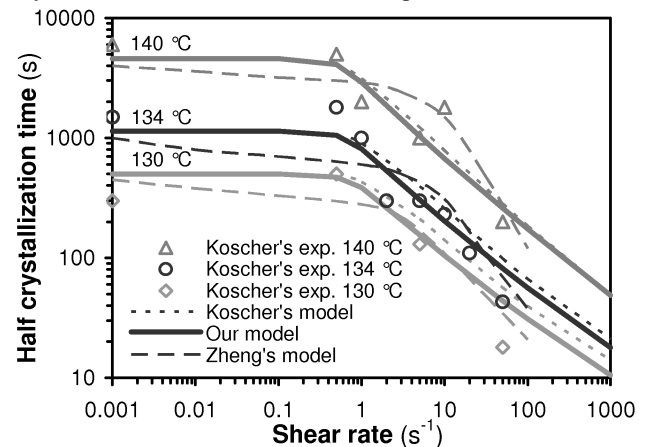


FIGURE 1 – COMPARISON OF CALCULATED (OUR MODEL, KOSCHER'S MODEL, ZENG'S MODEL) AND EXPERIMENTAL HALF-CRYSTALLIZATION TIMES VERSUS SHEAR RATE FOR SEVERAL CRYSTALLIZATION TEMPERATURES (SHEARING TIME : 10 S)

Moreover, our numerical results are very close to those obtained by Koscher et al. with their semi-analytical model. This was expected, since we have used many of their modeling assumptions (rheological behavior, quiescent crystallization kinetics) and the same material data. However, the introduction of a damping function and the use of a different flow-induced nucleation model can explain the deviation between our results and theirs when the shear rate increases. We have also plotted the numerical results obtained by Zheng et al. [21] for the same polymer. Slight discrepancies can be observed in the results, obviously because the two models are not based on identical assumptions. In Zheng's predictions, the crystallization kinetics enhancement is effective even for the lowest shear rates (lower than 1 s^{-1}) and the critical shear rate values are generally higher than ours. Nevertheless, the average deviation between the measurements and the calculations is equivalent for both models.

5.2. Isothermal 2D flow

In our model, the flow effect is taken into account by an enhancement of nucleation linked to the trace of the extra-stress tensor, i.e. the normal stress in pure shear flow. Fig 2 clearly explicit this relationship. The shearing intensity determines the maximal stress level and increase rate. As the strain grows, the relaxation modulus decreases because of the non-linear effects (damping function). Consequently, when the strain reaches some critical value, the stress begins to decay. Moreover, when the shearing stops, i.e. t_s is elapsed (Fig. 2), the stress decays more steeply, but doesn't relax instantaneously due to the fluid elasticity. This represents the polymer relaxation kinetics, which depends on the model chosen to describe its viscoelastic behaviour.

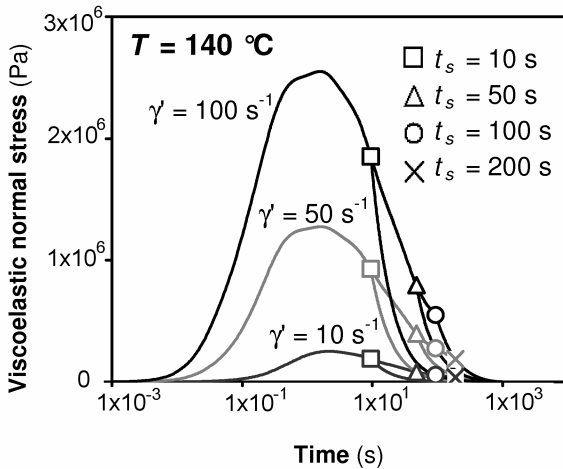


FIGURE 2– EVOLUTION OF THE VISCOELASTIC NORMAL STRESS FOR ISOTHERMAL CRYSTALLIZATIONS UNDER SEVERAL SHEAR RATES AND SHEARING TIMES (SYMBOLS INDICATE THE SHEARING TIMES)

Lets now analyse the effect of choosing a non lenar beaviour, and its discripeny to that obtained considering a linear viscoelstic one. After validation of the model in simple shearing flow, a 2D isothermal analysis is carried out.

For this configuration, a polymer melt, at a given temperature (140 °C), is considered flowing in an isothermal rectangular cavity, having 5mm thickness and 10 cm large. A parabolic velocity profile is imposed on the entrance zone during 2 seconds time, and then suppressed. The polymer flow stops after relaxation during a short time.

Figure 3 shows the fluid strain after a two second imposed inlet parabolic velocity, at several locations in the cavity with and without a damping function. As expected, the same flow displacement is obtained for the two models. It is imposed by the inlet conditions.

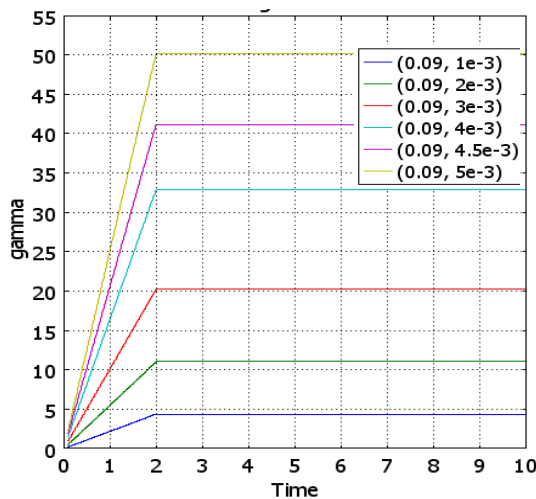


FIGURE 3– FLOW STAIN FOR SEVERAL LOCATION IN THE CAVITY THICKNESS

If we analyze the corresponding stress state generated by this flow. The same flows do not exhibit the same stress tensor, depending on considering a damping function to describe the rheological behavior of the fluid or no.

Figure 4 presents the evolution of the *trace* of the stress tensor versus time, in the case of a linear viscoelastic model, us assumed by Koscher. The same quantity is represented in figure 5, considering a non linear model (our model). In the first case, the *trace* of the stress tensor growth gradually as the inlet velocity acts. This means, that if the velocity continue for a long time, a very high value of the stress will be reached, and this value growth to infinity. It seems to be an aberration. By introducing a damping function, the relaxation of the fluid is then taken into account, and the evolution of the stresses becomes more reasonable. As the strain continue, the relaxation modulus decreases because of the non-linear effects, leading to a break down of the stress values when the strain reaches some critical value. When the flow is stops, the stress decays more steeply, but doesn't relax instantaneously due to the fluid elasticity. This represents the polymer relaxation kinetics, which depends on the model chosen to describe its viscoelastic behaviour.

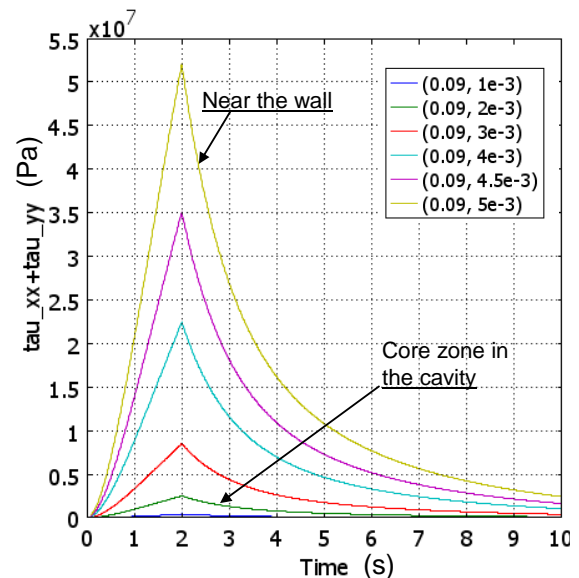


FIGURE 4– TRACE OF THE VISCOELASTIC STRESS TENSOR? AT DEFFERENT LOCATIONS IN THE CAVITY THICKNESS? WITH THE LINEAR MODEL

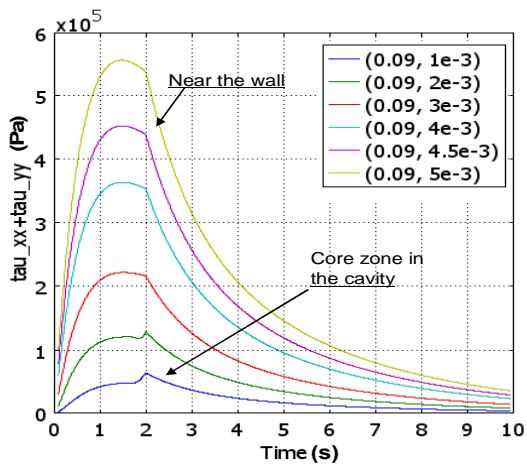


FIGURE 5– TRACE OF THE VISCOELASTIC STRESS TENSOR, AT DIFFERENT LOCATIONS IN THE CAVITY THICKNESS, WITH THE NON LINEAR MODEL (DAMPING FUNCTION)

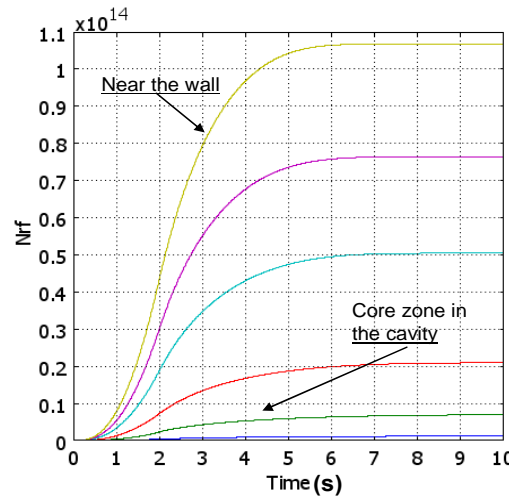


FIGURE 7– NUCLEATION DENSITY WITHOUT THE DAMPING FUNCTION

The damping function introduced into the model is an exponential function. For higher shearing stresses, the damping function value decreases quickly, and its effect on the flow is more important. As this function decreases, some modes in the Maxwell model become negligible. Near the wall, the shear rate is greater than in the core zone. For this reason, the evolution of the nucleation density versus time, presented in figure 6, shows that the crystallization induced by the flow is maximum close to the wall, where the stretching stresses are higher. If we compare the nucleation density calculated with the non-linear model, the number of nuclei is approximately two times less important than in the linear case, because of stress relaxation during the flow as illustrated in figure 7, where N_{rf} represents the number of flow induced nuclei.

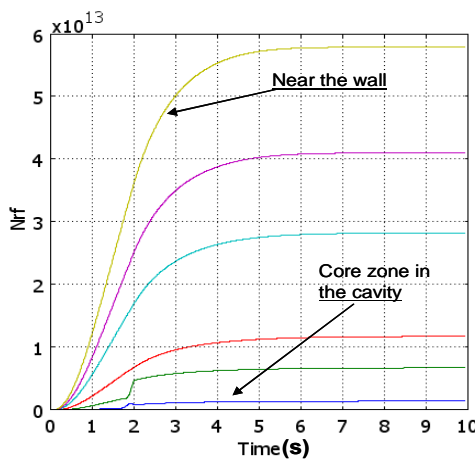


FIGURE 6– FLOW INDUCED NUCLEATION DENSITY WITH THE NON LINEAR MODEL (DAMPING FUNCTION)

5. CONCLUSION

In this work, a flow induced crystallization model is developed taking into account the viscoelastic behavior of semi-crystalline polymers.

Two distinct nucleation rates are considered. On one hand, the thermally induced nucleation rate corresponds to the nuclei that would be activated in quiescent conditions and only depends on the temperature level. On the other hand, the flow induced nucleation rate is linked to the trace of the extra-stress tensor, via a suggested empirical non linear relationship, which is a representative measure of the elasticity in the polymer melt, i.e. the orientation and stretching of the macromolecular chains.

The viscoelastic extra-stress tensor is calculated using the differential formulation of the Upper Convected Maxwell (UCM) model. The rheological behavior of the studied polymer (PP) is described by means of an eight mode relaxation spectrum and a damping function is introduced to account for the non-linear viscoelastic effects.

A comparison of stress tensors computed considering linear and non linear viscoelastic models shows that strong errors can be made, when assuming a linear behavior with large strain cases, as it was the case in several works related in the literature

The effect of this error impact strongly the crystallization rate induced by the flow, because it is linked to the chains orientation, due to the stress state generated by the flow.

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