

up to a thousand modules. No other model checker or other technique can handle this magnitude of state spaces.

References

- Kacprzak M., Lomuscio A., Niewiadomski A., Pęczek W., Raimondi F., Szreter M. (2006). Comparing BDD and SAT based techniques for model checking Chaum's dining cryptographers protocol. *Fundamenta Informaticae*, vol. 72(1-3), 215-234.
- Kacprzak M., Nabiątek W., Niewiadomski A., Pęczek W., Póroła A., Szreter M., Zbrzezny A., Woźna B. (2007). VerICS 2006 - A Model Checker for Real-Time and Multi-Agent Systems. *Proc. of CS&P'07*, 345-356.
- Lomuscio A., Pęczek W., Woźna B. (2007). Bounded model checking for knowledge and real time. *Artificial Intelligence*, 171, 1011-1038.

Institute of Computer Sciences
ul. Ordonia 21, 01-237 Warszawa
phone: 48 (022) 836 28 41
fax: 48 (022) 837 65 64
e-mail: ipi@ipipan.waw.pl
www. ipipan.waw.pl

Effects of crystallization on polymer processing with high deformation rates

L. Jarecki | Institute of Fundamental Technological Research | Polish Academy of Sciences

Crystallization is an important structural transformation influencing the dynamics of industrial polymer processing and controlling the physical and mechanical properties of the material. A physically sensible description of the transformation kinetics is needed for the computer modeling of industrial processes, which has become a standard technique in polymer technology. One distinct feature exhibited by polymeric materials is a strong increase in crystallization rate, by several orders of magnitude, caused by the deformation and orientation of the chain molecules. In industrial technologies involving melt processing, the chain deformation and orientation is usually controlled by time-dependent flow deformation and cooling. In fast processing, such as high-speed melt spinning, supersonic melt blowing, electro-spinning of fibers, the polymer fluid is often subjected to elongation rates of sev-

eral hundred times per second. Such fast deformations do not allow for relaxation of the molecular deformation and orientation during the processing time and, in crystallizing polymers, cause rapid stress-induced crystallization resulting in highly oriented texture shown in Fig. 1. The consequence of the high molecular orientation produced in such technologies is the strong enhancement of the mechanical properties of the polymeric products, often by orders of magnitude. Our research on this subject has focused on:

- modeling of the molecular deformation and orientation of polymeric fluids subjected to fast, time-dependent axial deformations (uniaxial, biaxial), as well as the kinetics of stress-induced crystallization,
- flow behavior of the polymer during crystallization (crystallinity-dependent viscosity),

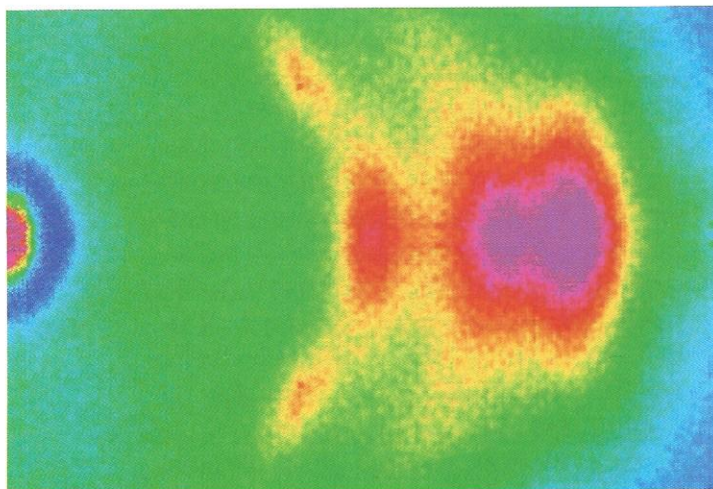


Fig. 1. Wide angle X-ray diffraction pattern illustrating high crystalline orientation of as-spun PET fiber

- effects of stress-induced crystallization in modeling of melt spinning of fibers, in particular the resulting limitation in the spinning speed and fiber thickness.

Molecular orientation and crystallization kinetics

We have proposed a theory of molecular deformation and orientation for fast flow deformations of polymeric fluids considering non-linear stress-orientation behavior and finite extensibility of flexible chain molecules. The approach remains valid in the entire range of the macroscopic deformation rates and deformations of the molecules from statistical coils to fully extended chains. The theory accounts for the molecular thermal motion, chain flexibility and flow convection of the chain molecules under the flow deformation. The time-dependent conformation distribution of the chain molecules,

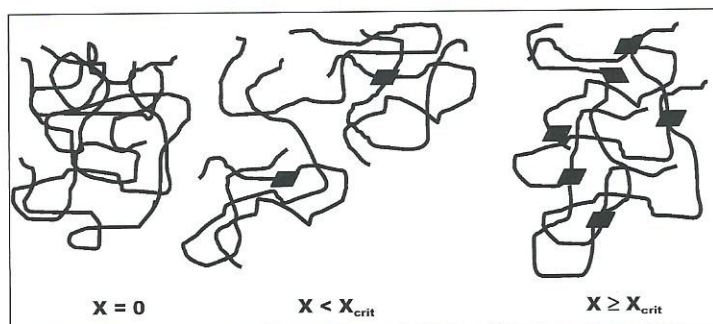


Fig. 2. Molecular model of crystallization affected viscosity. $X=0$ – entangled melt, $X < X_{crit}$ – crystal-bound aggregates, $X > X_{crit}$ – solid rubber-like network

as well as orientation distribution of the chain segments and free energy of the system, have been derived in mathematically tractable terms for time-dependent axial deformation rates. Time evolution of the characteristics is controlled by an instantaneous pseudo-affine molecular deformation with time-dependent axial chain elongation coefficients. The coefficients are given by a formula valid for the entire range of the deformation rates and stresses.

Parallel to the stress-orientation theory, a quasi-stationary kinetic theory of crystal nucleation in such systems has been proposed. The approach is based on an aggregation model proposed earlier by our laboratory for asymmetric particles and accounts for time-dependent segmental orientation and free energy of the system under the flow deformation. The asymmetric particles are identified with statistical chain segments. The kinetic theory predicts strong angular differentiation of the crystal nucleation rate, i.e. enhancement of nucleation rate by orders of magnitude in the orientation direction and reduction in the perpendicular direction. Both the non-linear stress-orientation theory and the quasi-stationary kinetic theory of nucleation are proposed for modeling of structural transformations in processes with high, time-dependent deformation rates.

Rheological behavior of the polymer fluid during crystallization

Rheological properties (viscosity, relaxation time) of polymer fluids are known to be sensitive to crystallization. A small amount of crystalline phase can make viscosity and relaxation time of polymer melts higher by orders of magnitude and convert the fluid into a plastic solid. This is visualized as physical cross-linking of the linear polymer chains by small crystals binding them together. When the number of such inter-chain bonds approaches a critical level in the course of crystallization, the polymer melt is converted into a solid rubber-like network, as illustrated in Fig. 2. The critical crystallinity X_{crit} can be as small as several percent. The abrupt increase in polymer viscosity near the critical crystallinity is represented by a hyperbolic function derived from the cross-linking theory. The hyperbolic, gelation-type formula has been used in modeling the dynamics and structure formation in melt spinning of crystallizing polymers.

Stress-induced crystallization in computer modeling of melt spinning

In the modeling, steady-state melt spinning is considered where the polymer melt is extruded from a spinneret orifice at a constant velocity V_0 and subjected to elongation and cooling along the spinning axis. At a distance L from the extrusion point, solidified filament is collected with a take-up velocity $V_L \gg V_0$. The computer model of the process is based on the mass, momentum, and energy conservation equations determining axial velocity, temperature, and tension profiles. Structure evolution equations account for stress-induced crystallization, and the constitutive equation accounts for polymer viscosity affected by local crystallinity and temperature. In a definite range of spinning conditions, when the stress-induced crystallization leads to rapid solidification of the polymer, bifurcation of the solution of the melt spinning equations is observed. The solution shows bifurcation if the take-up velocity V_L plotted vs. the initial tension force F_0 exhibits a maximum, as illustrated in Fig. 3. No fibers can be spun at speeds higher than the maximum. At the bifurcation, the same take-up velocity V_L leads to different velocity, temperature, and tensile stress profiles, as well as to different structures of the obtained fibers (amorphous or partly crystalline). The bifurcation determines the range of conditions necessary for stable formation of fibers and may be important for the design and optimization of the industrial processes. The practical significance of the predictions concerns limitations of the maximum spinning speed and the minimum of the filament diameter.

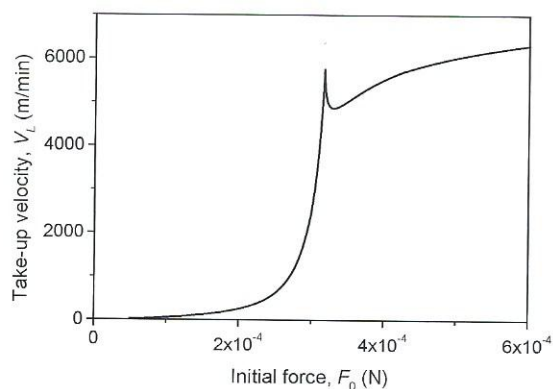


Fig. 3. The velocity-tension relation computed for melt spinning of PET

Critical conditions for bifurcation have been analyzed and the physical mechanism of such behavior has been discussed. The appearance of bifurcation is associated with the onset of crystallization. A necessary condition for bifurcation is the reduction of the polymer deformability along the spinning axis with increasing tension force. The reduction of deformability results from faster crystallization at higher tensile stresses combined with crystallinity-affected viscosity.

Temperature effects seem to be of lower, secondary importance. Bifurcation appears for polymers which crystallize slowly in the absence of the tensile stresses and change the crystallization rate by many orders of magnitude under high stresses. Three regions in the spinning speeds are consequences of bifurcation: spinning of amorphous fibers at low speeds, high-speed spinning of partly crystalline fibers, and the region of inaccessible supercritical speeds. The predicted regions are reasonably consistent with the experimental observations reported by other authors.

Stress-induced crystallization and crystallinity-affected viscosity are primary conditions for bifurcation. The impact of the primary conditions on the bifurcation can be reduced by suppressing the molecular orientation and stress-induced crystallization. This method consists in using immiscible polymer additives, desirably liquid-crystalline, which "take over" the internal stresses. The role of a secondary group of factors in spinline deformability, i.e. the molecular weight of the polymer, thermal conditions of the extrusion, and cooling, have been also discussed. At higher molecular weights the polymer starts to crystallize at lower spinning speeds, the maximum take-up velocity shifts to lower values, and the minimum filament thickness increases. We conclude that the melt spinning of super thin filaments is favored by application of low-molecular-weight polymers. Modification of the temperature of the ambient air provides an alternative important tool for increasing the accessible spinning speed and reducing the filament diameter, e.g. by introducing a hot tube on the spinning axis. We predict that an increase in tube temperature results in increased maximum spinning speeds and admitting much thinner filaments produced at higher speeds, inaccessible in classical high-speed melt spinning (Fig. 4).

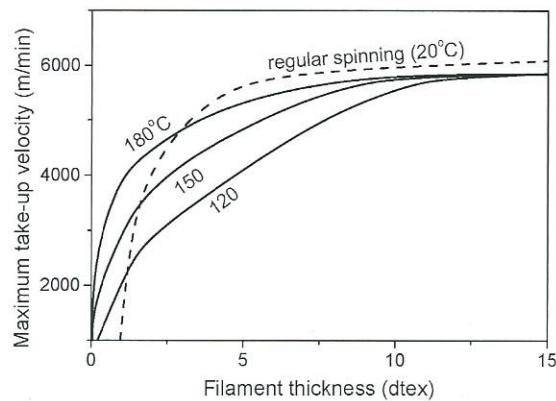


Fig. 4. Maximum take-up velocity vs. filament thickness computed for hot-tube melt spinning of PET at various tube temperatures (solid lines). Dashed line – classical spinning at room temperature

Concluding remarks

The mathematical modeling of structure transformations (orientation, crystallization) during melt processing of polymers with time-dependent, high axial deformation rates provides physically sensible formulations, valid in the entire range of the deformation rates and stresses. The formulations combined with computer modeling of the processing which involves stress-induced crystallization and structure-controlled viscosity can be adopted for other industrial techniques, with the aim of obtain-

ing super thin fibers with an industrial productivity rate. The subject may concern dynamics and structure formation in melt spinning under modified conditions, supersonic melt blowing of super thin fibers, electro-spinning of nano-fibers, etc. Further details of the theory and computer modeling are presented in the publications listed below.

References

- Jarecki L. (2007). In: *Progress in Understanding of Polymer Crystallization. Lecture Notes in Physics*, Reiter G., Strobl G.R. (eds.), Heidelberg, Springer, 65-85.
- Ziabicki A., Jarecki L. (2007). Crystallization-Controlled Limitations of Melt Spinning. *J. Applied Polymer Sci.*, 105, 215-223.
- Ziabicki A., Jarecki L. (2006). Structure-controlled bifurcation in mathematical modelling of fibre spinning. *Archives of Mechanics*, 58, 459-475.

Institute of Fundamental Technological Research
ul. Świętokrzyska 21, 00-049 Warszawa
phone: 48 (022) 826 12 81
fax: 48 (022) 826 98 15
e-mail: director@ippt.gov.pl
www.ippt.gov.pl

Modeling of polar ice sheet flows

R. Staroszczyk | Institute of Hydroengineering | Polish Academy of Sciences

Polar ice caps cover approximately 15 million sq. km of the Earth's surface in Antarctica and Greenland. The presence of such huge masses of ice has a significant impact on the global climate. Therefore, analyzing the thermo-mechanical processes taking place in polar regions is essential for understanding the dynamics of global warming.

A schematic cross-section of a large polar ice sheet is sketched in Fig. 1. An ice cap is typically up to 3-4 km thick and extends thousands of kilometers in lateral directions. During the passage from the glacier free surface, when the ice is formed in the accumulation zone, the material undergoes different

stress and deformation conditions. As a consequence, the initially isotropic free-surface ice gradually transforms into strongly anisotropic material in which the mechanical properties depend on the direction in space. Polar ice is a polycrystalline material and deforms mainly by viscous creep. The development of anisotropic structure (called *fabric*) in the highly deformed material results in the ice viscosities decreasing 5 to 10 times compared to the initial, isotropic ice values. For this reason, the anisotropy of ice, and its evolution, are important factors that must be taken into account when analyzing the overall flow of a glacier.