Skoltech Computational Materials Science Seminar



UHMWPE polymerization and fiber formation: computer simulations

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Objectives of modern material science



"Wet and soft" (biological systems, polymers, liquids, etc.)



Tree main contributions of polymer physics:

- 1. N monomers connected into united linear molecule, units can not move independently any more.
- 2. Number of monomer units is large, N >> 1.
- 3. Polymer chains are flexible and coiled.



Polymers lack of entropy!

Because of connected units polymer molecule has reduced translational entropy. That is the fundamental reason for polymers self-assembly: even small changes in energy could leads to great changes in conformation.





Ideal gas

What is most simple (and most complicated) polymer?

1933 LDPE. Spontaneous polycondensation of ethylene gas, at elevated temperature and pressure. Randomly branched molecules with large free volume and good film-forming properties.

1953 HDPE. Zigler and Natta: metallozene catalysis polyolefin polymerization. Nobel Prize in 1963.

1960 UHMWPE, MW > 1 mln g/mol

1970 UHMWPE fibers, 4-10 GPa. DSM (Netherland

2000 Homogeneous catalysis.

2022 Only a few world companies produce UHMWPE fibers, none in Russia.

Why?

...



Zwijnenburg/Pennings - 1976







linear





UHMWPE main property – the longest molecules (except DNA)

> 3 mln. g/mol (~100 000 monomer units)

Specific strength + softness





Рабочая нагрузка 10т вес 100 г. Рабочая нагрузка 3т вес 500 г.

That is because molecules length and orientation !



Chemical resistivity



Instant viscosity



Slipping

Polymer fiber – orientationaly ordered material.



Very different fibers have same orientation feature. But it induced by various techniques.

How to make oriented polymer fibers?



The main idea is very simple – mechanical transformation of chain conformations.

What prevents to obtain good fibers in an easy "from the melt" way?







Kevlar example – polymer with very strong interchain interactions



Сильные межмолекулярные взаимодействия:

- 1) T_{пл} > T_{хим разл} >400С
- 2) мало растворителей

Формование из раствора

Растворители – метилпирролидон + CaCl₂ (или серная кислота)



The only way to orient Kevlar molecules – great solvent excess.

UHMWPE – polymer without strong interchain interactions, looks like can be oriented without solvent great excess.

Main interactions – entanglements and crystallization.

That's because of entanglements it cannot be easily drawn!





What are the entanglements?

Untraceable and uncatchable entanglemets

They are not fixed in time and space, do not have specific spectroscopic signature, that is polymer material <u>topological property</u>!





«Entanglements length» Typical values around 50-100 units.

Most entanglements formed during polymerization process!

N_e almost impossible to measure in experiments, hardly possible to describe in theory, but can be computed in simulations: *Kroger, M. Comput. Phys. Commun. 2005, 168, 209.*



How to manage entanglements?

Dissolution in a small concentration after synthesis: expensive and environmentally sensitive

Entanglements control during polymerization process



NB: topoisomerase – Nature's way to solve entanglements problem in DNA.

Lab experiments





Rastogi et al, Macromolecules 2016, 49, 7497



Ziegler-Natta conventional polymerization



Single-site catalyst polymerization conditions for disentangled UHMWPE



What level of simulations should be selected to model UHMWPE?



Particle-based model + Large space and time scale = coarse-grained MD

БЭСМ-6, ВМК, 1970

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 31, NUMBER 2 AUGUST, 1959

Studies in Molecular Dynamics. I. General Method*

B. J. Alder and T. E. Wainwright

Lawrence Radiation Laboratory, University of California, Livermore, California

 $m_i \mathbf{a}_i(t) = \mathbf{F}_i(t) \quad [mass \times acceleration = force]$ $\mathbf{a}_i(t) = d\mathbf{v}_i(t)/dt = d^2 \mathbf{r}_i(t)/dt^2, \ \mathbf{F}_i(t) = -\partial U(\mathbf{r}_1, ..., \mathbf{r}_N)/\partial \mathbf{r}_i$





Ломоносов-1, ВМК, 2010



Algorithm:

- Calculate all particles positions (centers of applied force).
- 2. Calculate all forces.
- 3. Move particles.
- 4. Goto 1



European Conference on Computational Physics CCP 2001, Aachen (Germany)

A.Chertovich





Luo, Chuanfu, and Jens-Uwe Sommer. "Coding coarse grained polymer model for LAMMPS and its application to polymer crystallization." *Computer Physics Communications* 180.8 (2009): 1382

Meyer, Hendrik, and Florian Müller-Plathe. "Formation of chain-folded structures in supercooled polymer melts examined by MD simulations." *Macromolecules* 35.4 (2002): 1241

Part 1. polymerization.

Petrov, Kos, Rudyak, Chertovich, Macromolecules 53, 6796 (2020).



4 * 10⁵ steps, N = 1,9 * 10² Conversion 0,19%

 $1,6 * 10^{6}$ steps, N = 7,9 * 10^{2} Conversion 0,79% 1,3 * 10⁹ steps, N = 8,9 * 10⁴ Conversion 89%

Analytical model

Chains growth without entanglements in the beginning. As soon as growth up to $N_c(r, c)$ - entanglements starts to appear.

Results for critical chain length $N_c(r,c)$

Reaction conditions allow to control N_c . If we know $N_c(r,c)$ – we know $N_e(N,r,c)$. Mission completed: we can manage entanglements (in homogeneous polymerization).

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Analitycal theory vs. direct simulations

Theory is in a good agreement with N_e calculations!

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Part 2. Deformations.

NVT ensemble (ϵ =0.5), 10% of solvent (conversion 90%), Slow deformation, $T_{glass} < T < T_{cryst}$ ("cold drawing") *Petrov, Rudyak, Chertovich, Macromolecules*, 55, 6493 (2022)

Uniaxial deformation

Classical stress-strain deformation curve

Stress-strain curve typical of a low carbon steel (wikipedia)

Disintegration trigger – regime of entanglements duty

Analytical model of polymer melt deformation

No disentangling

Undeformed sample

Constant disentangling

$$\mathbf{Z} = Z_0 - 1 \qquad \mathbf{Z} = \mathbf{0}$$

event

 $\lambda_{max} \sim N/N_e$

Optimum point – no disentangling with minimum entanglements!

Optimum entanglements per chain:

Balance between disentangling and entanglements

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There is a great potential to increase fiber orientation!

Individual chains conformations

R(s) – distance in space vs. distance along the chain, sliding window averaging.

 $\begin{aligned} \mathsf{R} &= \mathsf{s}^1 - \mathsf{stiff} \text{ or stretched chain, "rod-like"} \\ \mathsf{R} &= \mathsf{s}^{0.5} - \mathsf{random walk} - \mathsf{Flory theorem} \\ \mathsf{R} &= \mathsf{s}^{0.3} - \mathsf{Crumpled or "fractal" globule} \end{aligned}$

Overall microscopy + 2DSAXS

A kind of shish-kebab only at elevated temperatures

Conclusions:

- 1. UHMWPE probably could be drawn into a well oriented fiber directly from the melt. For that one should learn how to control entanglements in a melt.
- 2. There is some optimal entanglements value $N_e = N^{3/5}$, which allow to obtain maximum oriented fibers. For typical UHMWPE (N=10⁵) it is around N_e =10³ (100 entanglements per 1 chain).
- 3. Nowadays samples are far away from that optimum value, so there is a prospect for further UHMWPE fiber strength improvement.

Publications:

- 1. Petrov, Kos, Rudyak, Chertovich, Macromolecules 53, 6796 (2020).
- 2. Petrov, Rudyak, Chertovich, Macromolecules, 55, 6493 (2022)

What next?

Open questions:

- 1. How deformations depends on temperature and pressure.
- 2. How orientation depends on deformation speed and boundary condition (Poisson ratio and simulation ensemble)

Possible tasks for next projects:

- 1. To create "hybrid" regime of drawing: disentangling of a sample exactly up to the optimal N_e.
- 2. To develop methodology of UHMWPE SLS: to predict optimal sintering conditions for a given N and $N_{\rm e}$.

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www.mspslab.com

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